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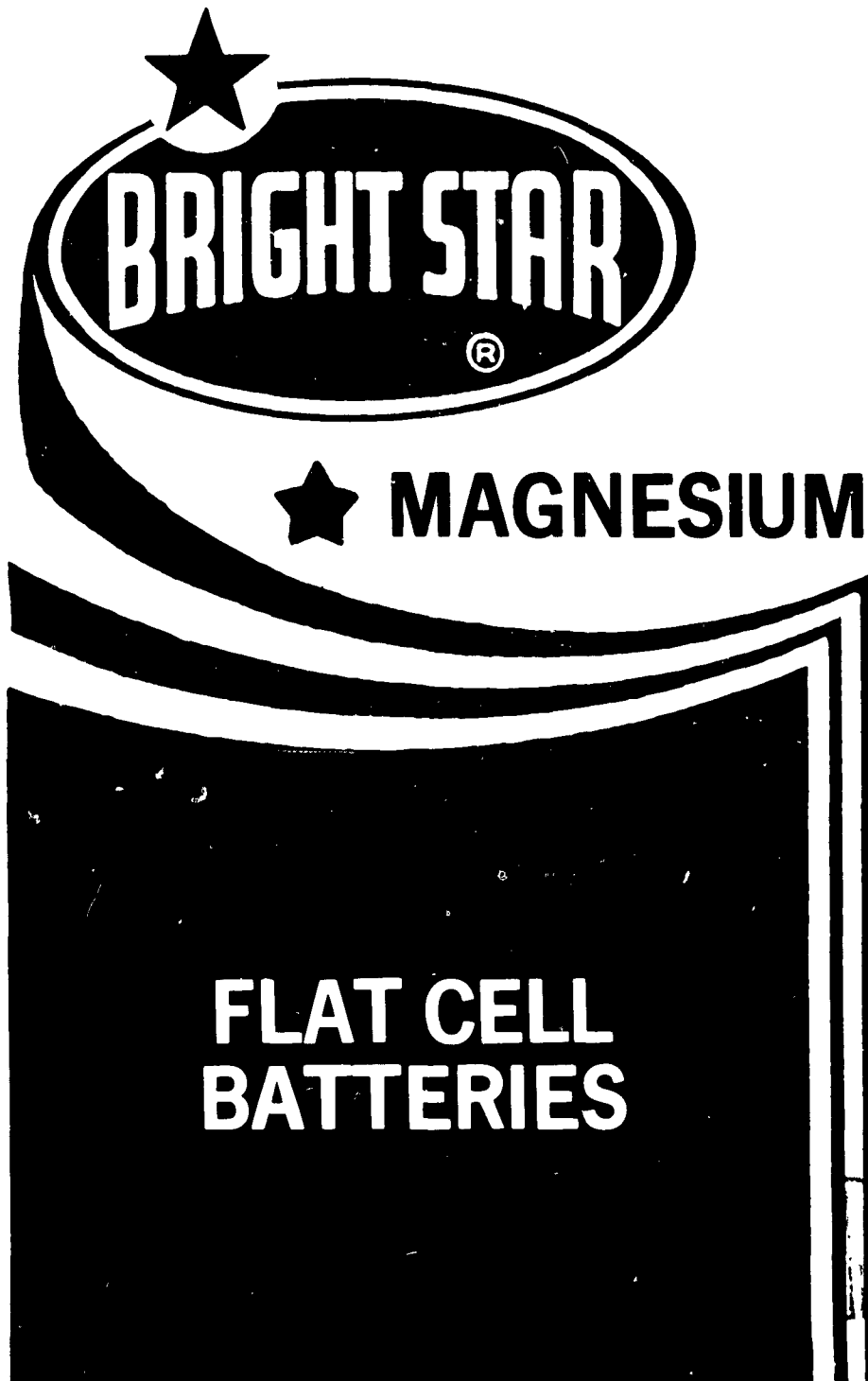
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MAGNESIUM FLAT CELL BATTERIES  
SIGNAL CORPS CONTRACT NO. DA-36-639-SC-78231  
DEPARTMENT OF THE ARMY  
TASK NO. 1G6 22001 A 053-02  
FINAL REPORT  
30 SEPTEMBER 1958 TO 30 OCTOBER 1963

PREPARED FOR  
U. S. ARMY ELECTRONICS RESEARCH and DEVELOPMENT LABORATORY  
FORT MONMOUTH, NEW JERSEY

SUBMITTED BY

BRIGHT STAR INDUSTRIES  
600 GETTY AVENUE  
CLIFTON, NEW JERSEY

FLAT CELL MAGNESIUM DRY CELL BATTERIES

REPORT 7

SIGNAL CORPS CONTRACT  
NO. DA-36-039-SC-78231

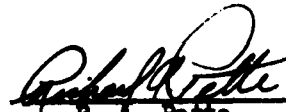
DEPARTMENT OF THE ARMY  
TASK NO. 1G6 22001 A 053-02

FINAL REPORT

30 SEPTEMBER 1958 TO 30 OCTOBER 1963

The objective of this research and development project is the development of magnesium flat cells and batteries in accordance with Power Sources Division Technical Guidelines for PR&C-ELS/D-3853 dated 30 January 1958.

Prepared by:

  
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BRIGHT STAR INDUSTRIES

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1. PURPOSE

Under Contract No. DA-36-039-SC-78231, Bright Star Industries agreed to conduct research and development work toward the development of magnesium flat cells and batteries in accordance with Power Sources Division Technical Guidelines for PR&C-ELS/D-3853 dated January 1958.

# ABSTRACT

Development of a  $\text{Mg/MgBr}_2/\text{MnO}_2$  flat cell battery was undertaken by Bright Star Industries, Clifton, New Jersey. This program was conducted during the period from 30 September 1958 through 30 October 1963.

Areas of investigation that received special attention were conductive coating of magnesium alloys, cathode mix formulations, duplex electrode and cell assembly techniques.

Increased capacity was obtained through adequate venting of hydrogen gas and proper choice of sealing materials. Capacity data on the effects of various parameters studied were obtained.

### CONFERENCES

The following conferences were held between representatives of the U. S. Army Signal Research and Development Laboratory and Bright Star Industries to discuss the program and progress for this period. Previous conferences are listed in the Semi-Annual Reports Nos. 1 - 6 of this contract.

<u>Date</u>	<u>Location</u>	<u>Representing USASRDL</u>	<u>Representing Bright Star Industries</u>
6-27-62	BSI, Clifton	A. Freer	F. Keller, H. Norman
8-1-62	BSI, Clifton	A. Freer	F. Keller, H. Norman
8-23-62	Ft. Monmouth	A. Freer, D. Wood	F. Keller
9-13-62	BSI, Clifton	A. Freer	C. Bishop, F. Keller, H. Norman
10-9-62	Ft. Monmouth	A. Freer, D. Wood	F. Keller
11-13-62	BSI, Clifton	A. Freer, D. Wood	F. Keller
1-18-63	Ft. Monmouth	J. Hovendon, A. Freer, D. Wood	J. Davis, F. Keller
2-27-63	BSI, Clifton	A. Freer	J. Davis, F. Keller, H. Norman, R. Pette
3-26-63	Ft. Monmouth	J. Hovendon, A. Freer, J. Murphy, D. Wood, J. Pawlak	J. Davis, R. Pette
5-8-63	BSI, Clifton	A. Freer	J. Davis, H. Norman, R. Pette
6-13-63	Ft. Monmouth	J. Hovendon, A. Freer	J. Davis, R. Pette
7-31-63	BSI, Clifton	J. Hovendon, A. Freer	J. Davis, R. Pette, H. Norman
8-20-63	Ft. Monmouth	J. Hovendon, A. Freer, D. Wood, J. Pawlak	R. Pette
9-29-63	Ft. Monmouth	J. Hovendon, D. Wood, J. Pawlak	R. Pette

#### 4. EXPERIMENTAL AND FACTUAL DATA

##### 4.1 GENERAL

Six semi-annual reports of this contract have been previously reported. The data therein and accumulated during this period are summarized in this final report.

Initial work on this contract was conducted to lead to the development of an efficient magnesium flat cell battery.

Further work was carried out to improve the initial performance and shelf life properties of the battery.

Areas of investigation which received special attention during this program are the following:

##### A. Research

1. Studies of conductive coating that are compatible with magnesium anodes.
2. Investigations of cathode mix formulation that afford optimum performance characteristics.

##### B. Development

1. The development of a flat cell meeting the BA-414/U requirements.
2. To develop techniques for rapid and economical assembly of magnesium flat cells into batteries.

#### 4.2 DESIGN

The initial dimensions and design for the flat magnesium 'N' cell and its components are as follows:

- a. Cell Cup: Cellulose acetate butyrate  
Tennessee Eastman Tenite II - No. 217A  
3/16 x 1 1/4 x 1 1/4 inches
- b. Duplex Electrode: Conductive coating - Glidden  
No. 95-103D  
Conductive film - Fassler No. 2 -  
0.008 inch  
Magnesium metal - AZ10, AZ21, AZ31  
alloys
- c. Separator: High purity kraft paper - 0.004 inch
- d. Depolarizer: 7% Shawinigan black - 50% compressed  
3% Barium chromate  
90% 300 African manganese dioxide
- e. Electrolyte: Magnesium bromide - 1.250 sp. gr.  
Lithium chromate - 0.3g/l
- f. Wetting Solution: Distilled water  
Triton 0.1%

In the following studies, the anode and cathode specifications are:

- a. Anode (duplex electrode):  
Size - 0.035 x 1.146 x 1.146 inches  
Weight - 1.55 ± 0.2 grams



b. Cathode (depolarizer cake):

Size - 0.140 x 1.0 x 1.0 inches

Weight - 4.0  $\pm$  0.1 grams

4.3 BATTERY ASSEMBLY

Cell Assembly:

The plastic cell cups were designed to fit together to produce a strong uniform stack of cells. In so-called stacked cell batteries, the anode of one cell is in juxtaposition with the cathode contact of the adjacent cell. Twelve cell cups containing eleven cathodes are stacked in series to produce a battery voltage of approximately 22.5 volts. A detailed drawing of the magnesium cell assembly is given in Figure 1.

Stack Assembly:

The twelve cup assembly is clamped and solvent sealed by dipping in ethyl acetate to bond the entire stack together. In the final step, the stack is dipped into a microcrystalline wax to provide a moisture vapor barrier.

4.3.1 Assembly Procedure

The initial N cell development is given in the following steps:

- a. Oxidation film was removed from AZ21XA magnesium alloy strip by sanding with aluminum oxide paper.

- b. One coat of Glidden conductive adhesive was applied and baked at 450°F.
- c. Strips laminated with Fassler No. 2 conductive film were blanked into duplex electrodes.
- d. Duplex electrodes were then pressed into molded N cell cups.
- e. A cupped kraft-paper separator was blanked and inserted into the cell cup.
- f. Mix cakes tamped on a Stokes press were placed into each cell cup.

All materials were produced with the specifications listed on page 2. Moisture content was kept to a minimum at wet mixing to prevent sticking of the mix cake to the tamping tools. Total electrolyte after assembly was 1.50 ml per cell. A noticeable amount of electrolyte leakage occurred due to the high percentage of moisture added at cell assembly. The following initial test data was recorded from stacks assembled as outlined above.

<u>Open Circuit Voltage (O.C.V.)</u>	<u>Short Circuit Amperage (S.C.A.)</u>
22.7	0.42
22.7	0.37

A Weston voltmeter, Model No. 24, with a sensitivity of 1000 ohms per volt and a Weston ammeter, Model No. 273, were used for routine measurements.

Cells were prepared by keeping the moisture at wet mixing to a minimum with an intermediate stage of storing the mix cakes in a high humidified atmosphere. Additional moisture was added using a micro-burette. Absorption of moisture by the mix cakes ranged from 0.51 to 0.76 grams. The difference in the amount of moisture content was wide and difficult to control. Stacks dissected for moisture analysis showed a range of 19.2 to 20.8 percent. Voltage and amperage data are given in Table I.

In view of the excessive drop in amperage, a mill mix containing ten percent Shawinigan carbon black was prepared. The three percent increase in black increased the cell moisture from 20 to 28 percent without external leakage. Test samples assembled for evaluation showed the following results:

	Open Circuit Voltage (O.C.V.)	Short Circuit Amperage (S.C.A.)
Initial	22.5	0.10
	22.6	0.15
1 Day	21.4	0.04
	21.8	0.05

Stack readings, after one day, displayed a sharp decline in amperage as did previous samples.

To study the effects of magnesium alloy corrosion, stacks were assembled with AZ31 duplex electrodes. Test samples indicated an excessive voltage and flash amperage decay after several days.

#### 4.4 Zinc Electrodes

Corrosion studies were made by replacing magnesium duplex electrodes with zinc anodes. Test stacks showed good voltage and flash current maintenance after two weeks. This indicated the carbon coating was corroding the magnesium alloys at the junction surface of the duplex electrode.

#### 4.5. Resistance Measurements

Lots were prepared with AZ21 and AZ31 magnesium anodes coated with carbon coating and Glidden No. 95-103D adhesive. Control samples with zinc anodes coated in the same manner were also assembled. Initial resistance measurements taken on the magnesium sample ranged from 0.5 to 1.5 ohms. After two weeks, the resistance increased between 9 to 45 ohms on both lots. Zinc duplex electrodes prepared with the same carbon vinyl coating showed a resistance of 1.4 to 1.9 ohms initially with little change after two weeks.

A search was undertaken to find a carbon coating which would not corrode magnesium alloys. A sample of conductive adhesive was obtained from F. P. Bartlett Company, Canton, Massachusetts. This material was designated as their No. F-134F coating. Test stacks were assembled with duplex electrodes prepared with Bartlett and Glidden adhesives and the following observation was noted:

#### Duplex Electrode Resistance

	<u>Bartlett Adhesive</u> <u>No. F-134F</u>	<u>Glidden Adhesive</u> <u>No. 95-103D</u>
Initial	0.3 - 0.5 ohms	0.5 - 1.0 ohms
1 Month	0.5 - 0.5 ohms	5.0 - 25.0 ohms
5 Months	3.5 - 7.0 ohms	72 - 200 ohms

It is apparent from the above data, the Bartlett conductive adhesive is more desirable for this type of application.

Stacks prepared with duplex electrodes containing Bartlett adhesive coatings were assembled for testing. Data showed an initial voltage of 23.5 volts with an amperage range of 1.3 to 1.5 amperes. Delayed readings, after sixteen days, declined to a range of 20.6 to 23.5 volts O.C.V. and 0.04 to 0.06 amperes S.C.A.

#### 4.6 Effect of Electrolyte Concentration

A study was made to determine the effect of various electrolyte concentrations on magnesium anodes.

Test stacks were assembled with AZ10 and AZ21 alloys using magnesium bromide electrolyte with different concentrations. Data given in Table II shows an excess of current decay due to the high resistance at the junction surface of the duplex electrodes after fourteen days.

A procedure was designed to protect the magnesium surface from corrosion by treating the AZ10 and AZ21 alloys in a pickling solution. The composition of this solution is given

below:

<u>Material</u>	<u>Amount</u>
Calcium chloride	0.1 grams
Magnesium nitrate	21.5 grams
Chromium trioxide	74.5 grams

Water added to make one liter

The magnesium alloys were submerged for two minutes at 200°F, then rinsed in hot water and air dried. The strips were then coated with various adhesives and laminated with Fassler No. 2 film. Magnesium duplex electrodes were blanked to a 1.058 inch diameter and cemented to a small plastic container with polystyrene dope. The container was filled with MgBr<sub>2</sub> electrolyte (1.200 sp. gr.) to a depth of 1/8 inch above the surface of the conductive film and closed with a rubber stopper. The apparatus was then stored at 70°F. Results obtained in the first week of testing showed that the Bartlett adhesive was superior to the Glidden material. The samples, assembled with magnesium treated in the pickling solution, showed a lower initial resistance and did not increase as steeply as compared with the sanded samples where the adhesive was applied directly to the magnesium.

The data for the studies described above are represented in Figure 2. In many of the samples tested, substantial deposits of magnesium hydroxide were built up on the surface of

the carbon film. A similar series of duplex electrodes without the electrolyte were run. This gave a more accurate determination of any changes taking place at the magnesium - adhesive - carbon film junction. By eliminating the electrolyte variables, any rise in resistance was attributed to the action of the adhesive on the magnesium alloy. Figure 3 shows the pickled samples averaged 4.8 ohms after three weeks as compared to 114 ohms for the sanded control samples. It is apparent from the above studies that the pickling process showed to be somewhat effective but did not afford total protection.

#### 4.7 Electroplating Zinc On Magnesium

A program was set up to determine the possibility of electroplating zinc on magnesium. Optimum results were obtained from coatings 0.0005 inches in thickness. Above this thickness, the coatings became unstable, tended to blister and flaked off readily. The maximum thickness obtainable did not afford adequate protection against the corrosive effects of the adhesive. Data recorded after one week showed the resistance averaging 13 ohms on zinc plated samples compared to readings of 500 ohms on control samples. The zinc plating technique was felt to warrant further investigation. The composition of the bath used is as follows:

<u>Material</u>	<u>Quantity</u>
Zinc cyanide	8 oz/gal.
Sodium cyanide	10½ oz/gal.
Sodium hydroxide	10½ oz/gal.

The bath temperature ranged between 35°C to 40°C with a current density of 15 ASF.

#### 4.7.1 Dow Electroplating Process

A series of experiments utilizing this process with several plating times was investigated. The process contains a complex series of operations which was outlined in the Third Semi-Annual Progress Report. The Glidden conductive adhesive was used to accelerate the tests as it has shown a higher corrosion rate on previous samples. The plating time ranged from 5, 10 and 20 minutes with a current density held at 15 amperes per square foot with an EMF of 3 volts. At seven days, the magnesium strips plated for 5 and 10 minutes showed an average of 3 - 5 ohms, samples plated for 20 minutes averaged 0.6 ohm. Figure 4 shows a control sample with Glidden adhesive applied directly to the magnesium vs. the 20 minute zinc plated samples. Test stacks were assembled using zinc plated duplex electrodes prepared by the Dow process. Stacks dissected after one week showed deep anode pitting and excessive corrosion going



through the magnesium to the carbon film. It appeared from the above studies that this condition is a result of the zinc plating operation.

#### 4.8 Bartlett High Purity Conductive Adhesive

Quantitative tests showed appreciable amount of chlorides present in the Glidden and Bartlett conductive adhesives. A sample of Bartlett high purity material was received and evaluated. Test stacks prepared with this material showed a sharp decline in voltage and amperage. Electrodes removed from these stacks ranged from 3 to 13 ohms in four days. In view of these results, the duplex electrodes were to be improved prior to battery assembly and test evaluation. Duplex electrodes prepared with AZ10 alloy, Bartlett high purity adhesive and Fassler No. 2 conductive film were assembled. Half the samples were placed in a humidior over magnesium bromide electrolyte, the remaining half were stored in polyethylene bags for control. Resistance of the control samples averaged 37 ohms after one week. It is apparent from the above studies that the high purity conductive coating is unsuitable for use in the magnesium cell.

#### 4.9 Dow Conductive Lacquers

The Dow conductive lacquer was designed for use in the magnesium flat cell. It was applied to the magnesium alloy

strip after sanding the surface for removal of oxides.

Four coats were applied by brush and baked for 20 minutes at 325-350°F. after each application. Total coating thickness averaged ten thousandths of an inch. This material maintained a low resistance at the junction surfaces although electrolyte penetration occurred after a few days.

An improved Dow conductive lacquer was developed and evaluated. Duplex electrodes were prepared in the usual manner. Electrodes stored at 70°F, 50% RH had an initial resistance of 0.2 ohm and 0.4 ohm at three weeks; electrodes stored over a magnesium bromide solution read 0.7 ohm at three weeks.

Four 11 cell stacks were assembled using the new Dow conductive coating and AZ10 alloy. The capacity data for these stacks are presented in Table III. Stack No. 2 displayed a lower voltage at the tenth day and was dissected for individual cell capacities.

Capacity data for the cells described above are presented in Table IV.

The procedure developed to apply the Dow lacquer to the magnesium alloy is as follows:

1. Sand surfaces of magnesium strip for oxide removal.
2. Apply lacquer to magnesium surfaces with a three inch mohair roller.
3. Continue to work material until coverage is complete.

4. Allow coating to stand approximately ten minutes until dry. Blistering may occur if baked too soon after applying coating.
5. Bake twenty minutes at 325° - 350°F.
6. Abrade surface with 3M aluminum oxide production paper "C" weight 3/0 - 120. This will remove blisters which may form during baking.
7. Remove excess dust and scrub thoroughly with 1N HCl solution. Rinse and dry. Acid treatment cleans small pin holes and improves wetting for additional coats.
8. Repeat above procedures between each application until six coats have been applied resulting in thickness of approximately .008 inch.
9. Apply one coat of Bartlett conductive adhesive in order to bond with plastic cell cup.

Six 11 cell stacks were assembled to evaluate the suitability of the Dow lacquer for a duplex electrode in magnesium flat cell batteries. Test results are given in Table V.

#### 4.10 Dow No. 3 Conductive Coating

Six coats of the Dow coating were applied and baked for twenty minutes at 325° - 400°F. between each application.

Cells were wet with magnesium bromide electrolyte 1.250 sp. gr. to a total water content per cell of 1.50 grams. Stacks were kept in a humidor after assembly for three days, solvent sealed and returned to the humidor for additional degassing prior to waxing on the sixth day. No wax blisters occurred using this method. Test results for six stacks are given in Table VI.

Visual observation of stack No. 1 showed excessive anodic corrosion at the edge of the magnesium extending into the window of the cell cup. This effect was due to electrolyte creepage at the edge of the anode making contact with the cathode of the adjacent cell. This condition was caused by poor sealing of the duplex electrode to the cell cup. Data obtained for individual cells in stack No. 1 are given in Table VII. These results show five cells failing to maintain capacity after sixty days.

In view of the above, additional studies were made to determine the corrosive effect of the new Dow coating. Data for these stacks are presented in Table VIII. Evaluation of the duplex electrodes at 7 1/2 days showed resistance of 0.5 to 1.5 ohms. The Dow No. 3 conductive coating was noted to be superior to previous materials investigated.

#### 4.11 Dow Conductive Coating With Polyethylene Gasket

A program was set up to determine the limitations of the duplex electrode seal. Single polyethylene gaskets blanked from 0.010 inch sheets were placed between the cathode side of the duplex

electrode and the cell cup. Assembly of this method is given in Figure 5. The assembly was heat sealed at 365°F on an Arbor press for six seconds. From the beneficial effects of thermally forming a gasket from the cathode side of the duplex electrode, the following experiments were run:

- a. Stacks (Nos. 1-8) were assembled with duplex electrodes containing three coats of Dow No. 3 conductive coating and one coat of Bartlett adhesive were thermally sealed in polyethylene gasket cell cups.
- b. Stacks (Nos. 9-16) were assembled with duplex electrodes containing three coats of Dow No. 3 conductive coating and one coat of Bartlett adhesive. A 13/16 inch diameter disk of Fassler No. 2 conductive film was heat sealed to the cathode side of the duplex electrode at the cell cup window. This assembly was thermally sealed in polyethylene gasket cell cups.

In this assembly, the Dow coating was employed to protect the magnesium surface from corrosive effects of the Fassler film. This film was used to prevent inter-cell penetration of electrolyte.

Resistance measurements ranged from 0.5 to 1.0 ohm on electrodes used in stacks 1-8, and 0.5 ohm or less in stacks 9-16. This effect is apparent when one notices the similarity in the open circuit voltage in comparison to the wide range in flash current data given for the two lots in Tables II and I.

Studies employing different techniques of applying various conductive films directly in contact with magnesium anodes were carried out. Evaluation of several techniques showed high resistances at the surface junction of the duplex electrodes. Examination of individual cells indicated extensive anode corrosion due to electrolyte penetration of the conductive film disk.

#### 4.12 Charlotte Colloidal Mill

Previous experiments in which the particle size of the Dow No. 3 conductive coating was noted to be large, noticeable amounts of the conductive material separated readily from the vehicle. A study was made with this material after being passed through a Charlotte colloidal mill several times. Stacks were assembled with duplex electrodes having three coats of conductive material and a polyethylene gasket thermally sealed to the cell cup. This procedure showed no improvement as electrolyte penetration occurred through the conductive coating after two months. Control stacks assembled for evaluation of the Fassler film and polyethylene gasket showed normal voltage and flash current after 128 days. The test data for this study are presented in Table XI. The data illustrate the advantage of the Fassler No. 2 conductive film over previous methods. The combination of this film with three coats of Dow No. 3 coating and thermally sealing the anode assembly with a polyethylene washer offered an efficient magnesium duplex electrode.

#### 4.13 Metal Jacket Studies

Observation of stacks discharged previously showed evidence of cell separation at the cup joint. A method of binding stacks to resist expansion caused by discharge reaction products was investigated. A 0.010 inch tin plate cover was designed to jacket the battery and enclose brass terminal plates for connectors. The terminals were held in contact with the magnesium surface by insulating washers and jacket crimp. Duplex paper (30-30-30) was used to insulate the stack from the metal jacket. Studies employing the metal jacket in stack assembly were carried out, the results are summarized in the following sections.

#### 4.14 Evaluation Program

- A. Testing The following testing and storage conditions were set up to evaluate the development of the BA-414/U magnesium flat cell battery:
1. 3100 ohm continuous
  2. BA-414/U intermittent (1300 ohms for 2 minutes, 3300 ohms for 18 minutes; 4 hours per day, 5 days per week).
- B. Storage The following conditions of shelf life and service maintenance were set up:
1. 70°F, 50% RH - Initial, 1, 2 and 3 months
  2. 113°F, 50% RH - Initial, 1, 2 and 3 months

#### 4.15 Initial Capacity Study

Sixty 11 cell stacks were assembled to determine the capacity of the BA-414/U battery incorporating the duplex electrode assembly given in section 4.11, procedure b. The cells were fabricated with the following cathode mix formulation:

<u>Material</u>	<u>Amount</u>
Manganese dioxide (African)	87.0 g.
Shawinigan carbon black 50% compressed	10.0 g.
Barium chromate	3.0 g.
Magnesium bromide electrolyte (1.250 sp. gr.)	1.5 g.

Average initial and tropical storage data is given for stacks discharged at a 3100 ohm continuous drain to 16.5, 15.0 and 13.5 cut-off points in Table XII. Average test data for the BA-414/U drain is summarized in Table XIII. Capacity data to a 16.5 volt cut-off is presented in Figure 6.

It will be noticed that low initial service of 26 hours was obtained from the BA-414/U drain. This can be attributed to the use of natural ore depolarizers in the cathode mix.

#### 4.16 Cathode Mix Studies

A program was initiated to study the discharge characteristics of the BA-414/U battery employing the use of synthetic manganese dioxide. Manganese Chemicals Type "M" and Bright Star electrolytic manganese dioxide were chosen for this study. Three ratios of manganese dioxide to carbon black to barium chromate were



selected initially for the Type "M" MnO<sub>2</sub>. Cathode mix formulations for these mixes are given as follows:

4.16.1 Type "M" MnO<sub>2</sub>

	<u>Material</u>	<u>Amount</u>
a.	Type "M" MnO <sub>2</sub>	89.0 g.
	Shawinigan carbon black 50% compressed	10.0 g.
	Barium chromate	1.0 g.
	Wetness per/1000 g. dry mix:	231 ml. MgBr <sub>2</sub> (1.250 sp. gr.) with 0.3 g/l Li <sub>2</sub> CrO <sub>4</sub>
b.	Type "M" MnO <sub>2</sub>	85.0 g.
	Shawinigan carbon black 50% compressed	12.0 g.
	Barium chromate	3.0 g.
	Wetness per/1000 g. dry mix:	264 ml. MgBr <sub>2</sub> (1.250 sp. gr.) with 0.3 g/l Li <sub>2</sub> CrO <sub>4</sub>
c.	Type "M" MnO <sub>2</sub>	89.0 g.
	Shawinigan carbon black 50% compressed	8.0 g.
	Barium chromate	3.0 g.
	Wetness per/1000 g. dry mix:	220 ml. MgBr <sub>2</sub> (1.250 sp.gr.) with 0.3 g/l Li <sub>2</sub> CrO <sub>4</sub>

Bromine vapors were evolved when wet mixed with magnesium bromide electrolyte indicating the activity of the Type "M" MnO<sub>2</sub>. Test stacks were assembled and discharge characteristics were determined at 3100 ohm continuous and BA-4114/U intermittent drains. The capacity data are given in Tables XIV and XV. The results are compared in Figure 7.

#### 4.16.2 Bright Star Electrolytic MnO<sub>2</sub>

<u>Material</u>	<u>Amount</u>
Bright Star El MnO <sub>2</sub>	87.0 g.
Shawinigan carbon black 50% compressed	10.0 g.
Barium chromate	3.0 g.
Wetness per/1000 g. dry mix:	273 ml. MgBr <sub>2</sub> (1.250 sp. gr.) with 0.3 g/l Li <sub>2</sub> CrO <sub>4</sub>

Stacks employing Bright Star electrolytic MnO<sub>2</sub> showed excessive electrolyte leakage at solvent sealing. This effect was caused by the increase in electrolyte added at cell assembly. Moisture content was found to be extremely critical, ranging in the higher absorption levels with the Bright Star electrolytic MnO<sub>2</sub> in comparison with the Type "M" MnO<sub>2</sub>. Consequently, the total electrolyte per cell was reduced from 1.80 to 1.70 ml. MgBr<sub>2</sub> (1.250 sp. gr.). Capacity data for stacks discharged on the BA-414/U intermittent drain are given in Table XVI.

#### 4.17 Thirteen-Cell Stacks

Evaluation of the discharge curves for the African manganese dioxide (87-10-3 formulation) indicate an increased cell complement. Approximately 3½ times more capacity was obtained to the 13.5 volt cut-off compared to the 16.5 volt cut-off when discharged on the BA-414/U intermittent drain.

Three lots to evaluate the capacity of the 13 cell stack were prepared. Manganese Chemicals Type "M" MnO<sub>2</sub> with the addition of magnesium hydroxide used in the cathode mix composition is given as follows:

<u>Material</u>	<u>Amount</u>
MnO <sub>2</sub> (Type "M")	87.0 g.
Shawinigan carbon black 50% compressed	10.0 g.
Barium chromate	3.0 g.
Magnesium hydroxide	1.0 g.
Wetness per/1000 g. dry mix:	242 ml. of MgBr <sub>2</sub> (1.250 sp. gr.) with 0.3 g/l Li <sub>2</sub> CrO <sub>4</sub>

Mix cake thickness was reduced to 1.15 - 1.25 inches to maintain the overall height for the BA-414/U battery specifications. Evaluation of the discharge data showed that no improvement in capacity over the 11 cell stack was obtained when tested at identical conditions.

#### 4.18 Hydrogen Venting

Previous experiments showed early rupturing of cell cups due to inadequate venting of hydrogen gases. Discharge data obtained from stacks using Type "M" manganese dioxide indicated that all fell below the 16.5 volt cut-off during the first 30 hours of testing. Capacity data for the BA-414/U drain is given in Table XVII.

Stacks exhibiting low voltage readings were vented by piercing the cell with a heated stellite needle below the cup joint. In cases where hydrogen pressures were vented prior to cell rupturing, voltages recovered to a normal level and good capacities were obtained. Stacks stored under tropical storage conditions (113°F, 50% RH) indicated a greater tendency toward this condition.

Studies of several methods of relieving the internal pressure in the cell cups were investigated. Stacks were prepared to study the effects of hydrogen venting by piercing the plastic cup with a stellite needle. Vent holes were covered with Scotch acetate tape No. 711 (3M Mfg. Co.) and stacks were dipped in microcrystalline wax. Three stacks on initial testing showed a 50 percent increase in capacity over control samples that were not vented. This performance illustrated the advantage of venting the stacks during assembly. In view of the above, further emphasis was put on improving hydrogen venting and assembly techniques.

#### 4.19 Single Channel Cell Cups

A plastic (cellulose acetate butyrate) cell cup was designed having a ten thousandths inch thick section in one corner which, when internal pressure developed, would rupture and give a "Bunsen" valve effect. Cell cups molded incorporating the gas venting channel were assembled into test stacks. Evaluation of the test stacks showed that the single gas channel did not give the desired venting action. Voltage readings during discharge indicated a sudden drop below test cut-off and recovery at a later period. This effect is due to an increase in internal pressure at a position farthest from the channel vent. The vent remains ineffective until a substantial amount of pressure builds up which increases the internal resistance of the cell

indicated by a sudden sharp decline in discharge voltage.

#### 4.20 Three Channel Cell Cups

As a result of the observations made above, cell cups incorporating two additional venting channels was designed. A fourth channel was not possible due to the location of the plastic feeding channel in the mold.

A lot using Tenite II cups with three venting channels was assembled as the previous experiment. Stacks discharged initially indicated that the venting channels were not functioning as anticipated. Initial capacity on the BA-414/U drain averaged 17.6 hours with a range of 48 hours.

#### 4.21 Ethyl Cellulose Cell Cups

The study of hydrogen venting was continued using an ethyl cellulose cell cup with three venting channels. Test stacks were assembled as the previous lot. Discharge data indicated an average of 40 hours with a range of 20 hours and an abnormal drop in amperage at one month. Duplex electrodes removed showed a resistance of 1.5 ohms or less. Further examination gave evidence of excessive edge corrosion on several electrodes. Bonding between the cell cup and polyethylene gasket during cell assembly was inferior to the butyrate cup. Experiments using methyl ethyl ketone as a solvent for ethyl cellulose cell cups were studied. Test stacks assembled were

dipped at various solvent seal times. Results showed a poor performance in comparison to control samples using ethyl acetate solvent seals. In most cases, poor bonding was noticed at the cup joints resulting in external electrolyte leakage. Waxing showed little or no improvement since there was poor adhesion to the plastic cup.

#### 4.22 Solvent Seal Studies

A program was initiated to study cell cup bonding with respect to shelf life capacities using controlled solvent seal conditions. A cathode mix consisting of Type "M"  $\text{MnO}_2$  and magnesium hydroxide as a buffer was prepared. Previous studies indicated that the Type "M"  $\text{MnO}_2$  is desirable for the BA-4114/U discharge requirements.

The cathode-mix composition used was as follows:

<u>Material</u>	<u>Amount</u>
$\text{MnO}_2$ (Type "M")	86.0 g.
Shawinigan carbon black 50% compressed	10.0 g.
Barium chromate	3.0 g.
Magnesium hydroxide	1.0 g.
Wetness per/1000 g. dry mix:	247 ml. $\text{MgBr}_2$ (1.250 sp. gr.) with 0.3 g/l $\text{Li}_2\text{CrO}_4$

Cellulose acetate butyrate cell cups were chosen for initial studies due to the poor performance of the ethyl cellulose cups as indicated previously. Solvent seal studies with ethyl acetate at different time intervals were carried out. The procedure

used for test lots prepared for this study is as follows:

Lot No. 1 - Six second dip and air dry.

Lot No. 2 - Three second dip, ten minute air dry,  
three second dip and air dry.

Capacity data for Lot No. 1 on initial testing showed improvement over previous solvent sealing conditions. Figure 8 shows the lower and often erratic discharge voltage of Lot No. 2. This evidences the difficulty of hydrogen venting as previously mentioned. In view of the above, solvent seal time was increased to a nine second dip using the same cell cup material. Capacity data in Figure 9 shows the improved performance of this method at initial testing. For solvent seal times greater than nine seconds, discharge data showed poor voltage regulation due to excessive electrolyte leakage with deep pitting of the cell cup.

Further determinations made with various solvent conditions are summarized in Table XVIII. The data shows that good capacity is obtained at the nine second dip using the butyrate cup while the voltage range is quite small. Excessive terminal corrosion of the brass connectors was present when stacks showed evidence of external electrolyte leakage. An increase in terminal resistance caused a premature voltage drop below the cut-off point to occur. A study was made using Zilloy No. 203 (New Jersey Zinc Company) end connectors to reduce the amount of terminal corrosion to a minimum. Examination of stacks, after testing, showed a marked reduction in terminal corrosion with

those using the Zilloy connectors.

As stated previously, poor discharge performance is indicative of inadequate hydrogen venting techniques. Stacks discharging at longer periods show physical separation of stacks at cell cup junction. This condition was due to poor intercell bonding when the cell assembly was solvent sealed. Methods of producing a stronger stack at cell assembly were sought.

Stacks solvent sealed in ethyl acetate for nine seconds were wrapped with two strips of fibre glass tape. Tin plate terminals used as end connectors were held between the end cell cup and the tape. Stacks discharged initially on the BA-414/U drain showed a maximum capacity of 72 hours. The glass tape, when properly applied, offered a stronger and more uniform stack under discharge. However, a large number of failures resulted when the tin plate strips were not properly secured to the magnesium metal.

A 5 percent solution of butyrate resin in ethyl acetate was prepared for solvent sealing. Lot A dipped for nine seconds and Lot B dipped for forty-five seconds were compared for bond strength. Test data recorded for Lot A averaged 80 hours with a range of 10 hours. Lot B averaged forty-nine hours with a range of 60 hours and showed a poorer performance in which several stacks displayed erratic voltage drops as early as 24 hours after discharge. This effect indicates the difficulty in hydrogen venting as this group was solvent sealed five times longer than



Lot A. Visual inspection of stacks, after discharge, showed a thin film of butyrate plastic enveloping the entire stack. The 20 percent increase in performance obtained can be attributed to the additional bond strength and moisture barrier afforded by this method.

Capacity data obtained for stacks dipped in 10 percent solution of butyrate resin in ethyl acetate indicated an average increase of 10 hours service over the previous experiment. Discharge data averaging 90 hours on the initial BA-4114/U intermittent drain is given in Figure 10. Data obtained for stacks after 3 month tropical storage is shown in Figure 11. The discharge curve for the stack reaching a maximum capacity of 100 hours at initial testing is given in Figure 12.

Further studies using more viscous butyrate solutions indicated a poorer performance on discharge. Thicker coating of the plastic tends to hinder proper venting of the cells. Figure 13 shows the poorer performance obtained from stacks dipped in a 20 percent butyrate solution for nine seconds.

#### 4.23 Moisture Seal Studies

In an attempt to improve shelf life characteristics, a study was carried out to find an improved moisture barrier material. A literature search indicated that polyethylene resin added to microcrystalline wax would provide an efficient moisture seal. Inspection of stacks coated with wax mixtures of polyethylene copolymers showed that the waxes became brittle and

cracked within several weeks. Evaluation of hot wax seals to butyrate cups showed that hard waxes had little adhesive strength. Although better adhesion was obtained with the softer materials, these are undesirable for elevated temperature storage. Best results were obtained by dipping the stacks twice for a one second period at 275°F. The formulation of the sealing compound presently used is as follows:

<u>Material</u>	<u>Amount</u>	<u>Company</u>
Microcrystalline wax	19 lbs.	Baresco Company
Resin wax	1 lb.	Borden Chemical Company
Defoamant oil	4 drops	Socony Mobile Company

Moisture barriers, other than waxes, were investigated. Samples of materials received from various companies were tried. Table XVIII shows the material, method of application and average service obtained. Control samples prepared with 10 percent butyrate solution are compared.

The following conclusions can be drawn from an examination of the experimental data obtained:

- a) Good gas barriers such as vinylidene chloride copolymers cannot be used as an efficient moisture barrier due to poor hydrogen venting control.
- b) Aqueous emulsions, such as the Dow latex and Rohm & Haas Rhoplex R-9, offer no reinforcement to the cell assembly.

- c) Silicone cements used showed poor discharge performance due to inadequate bonding properties to the butyrate plastic.
- d) Materials that will bond to butyrate plastic offer additional strength and a good moisture barrier to the cell assembly.
- e) Compatible materials, such as butyrate resin itself, provides additional bonding strength and an efficient moisture barrier as well.

As a result of the observations made above, samples of butyrate plastic cement (No. 5576) and butyrate thinner (No. 5577) were obtained from Tennessee Eastman Company. Both solutions contained methyl celluloseacetate which increased the drying times of the solvent seal operation. Accordingly, studies were conducted at various sealing time. Stacks dipped in 10 percent solution longer than seven seconds showed external electrolyte leakage, under six seconds, stacks exhibited poor bonding quality. The optimum dip time in butyrate thinner is six seconds. The data in Figure 14 illustrates the advantage of the butyrate cement over the previous solutions prepared with ethyl acetate in that it reduces the amount of pitting to the cell cup. It must be noted that the superior bonding quality of the butyrate cement and thinner lies in its compatibility with the butyrate cell cups.

#### 4.24 Shelf Life Studies

To increase the shelf life of the magnesium flat battery developed thus far, magnesium perchlorate electrolyte was studied since it is less corrosive to a magnesium anode than either a magnesium chloride or a magnesium bromide electrolyte. Also, magnesium has a low level of static corrosion in a perchlorate electrolyte, thereby insuring a good shelf life for dry cells<sup>1</sup>. Magnesium flat cells were fabricated with the following cathode mix formulation:

<u>Material</u>	<u>Amount</u>
Manganese dioxide (Type "M")	86.0 g.
Shawinigan carbon black 50% compressed	10.0 g.
Barium chromate	3.0 g.
Magnesium hydroxide	1.0 g.
Wetness per/1000 g. dry mix:	274 ml. $\text{Mg}(\text{ClO}_4)_2$ 250 g/l with 0.3 g/l $\text{Li}_2\text{CrO}_4$

In addition, duplex electrodes were assembled using a silicone cement (General Electric Company, No. RTV-102) to bond the anode to the cell cup. Figure 15 shows the data for previous studies using the bromide electrolyte incorporating the silicone cement bond. Stacks averaged 94 hours on the BA-414/U drain with little electrolyte leakage noticed.

As of this writing, shelf life studies with the perchlorate electrolyte using the cathode mix composition listed above are presently being conducted at the U. S. Army Electronics Research and Development Laboratories, Fort Monmouth, New Jersey.

<sup>1</sup>RCA Final Report titled High-Capacity Magnesium Batteries.

### CONCLUSIONS

Good performance of magnesium flat cell batteries was not obtained until several problems were overcome.

Choice of a suitable conductive coating was limited to those of a high purity content. Most commercially prepared carbon coatings investigated contained impurities which made them unsuitable for use in the magnesium cell. Initial anode corrosion, due to electrolyte penetration of the cell cup seal, was very extensive. This resulted in a poor discharge performance with little or no cell capacity obtained after a few weeks of shelf life. Thermally sealing the duplex electrode assembly to the cell cup with a polyethylene gasket greatly increased the overall performance of the battery.

The discharge results obtained from the equivalent BA-414/U drain are quite promising, an average of 93 hours being obtained when tested initially at 70°F., 50% R.H. Results obtained after 3 months tropical storage conditions (113°F., 50% R.H.) averaged 45 hours indicating a 50% capacity retention compared to those tested initially.

At the present state of development, the magnesium flat cell stacks have a limited shelf life when subjected to tropical storage conditions. Improvements in the moisture barrier and cell cup materials would improve the capacity retention over a large temperature range.

### RECOMMENDATIONS FOR FUTURE WORK

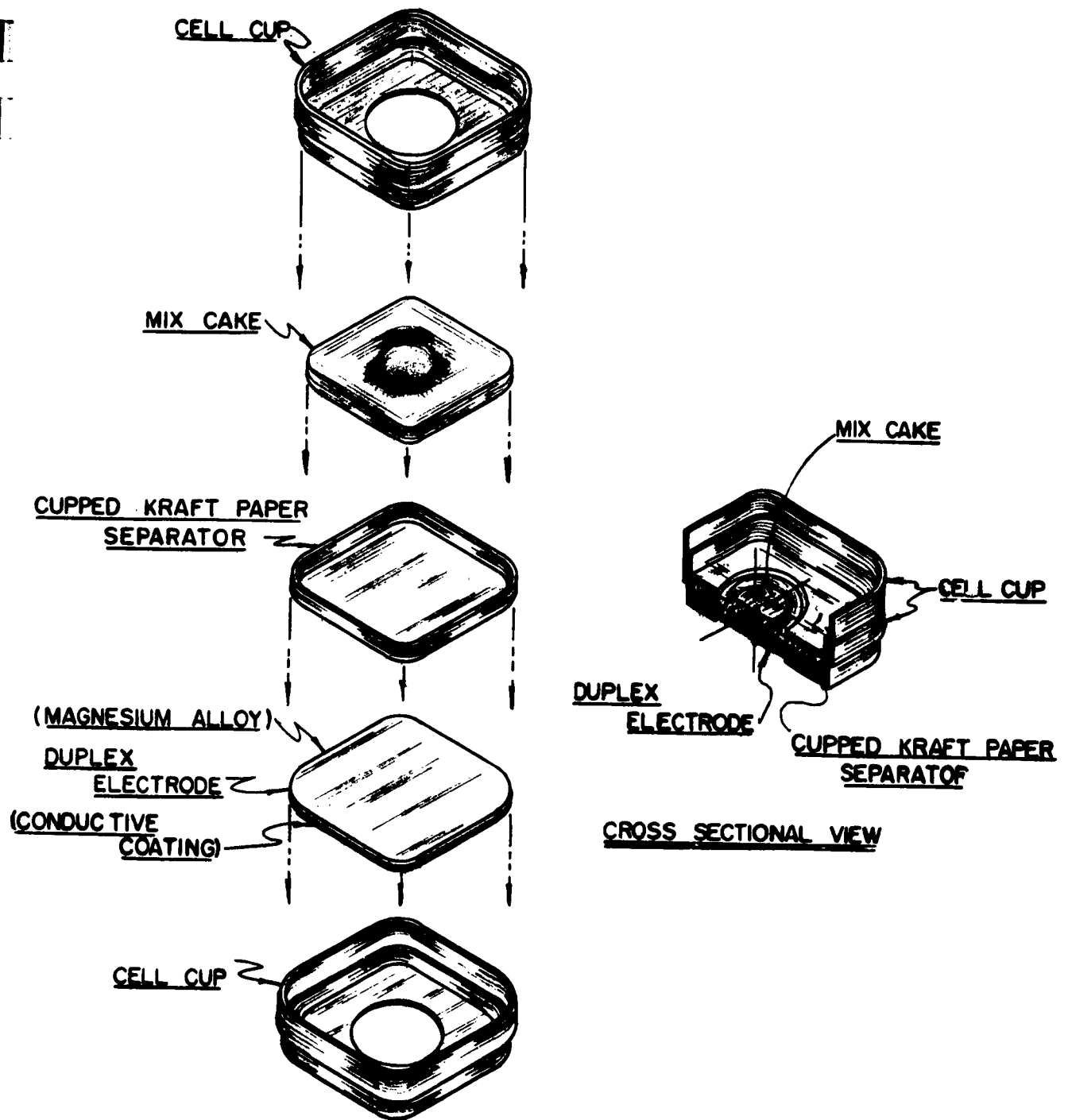
Methods of increasing the shelf life capacity of magnesium flat cell batteries should be further investigated.

Molding cell cups with polyethylene would show the following beneficial effects:

1. Material has a low water vapor transmission rate.
2. Cells can be heat sealed, thereby reducing the ill-effects of solvent sealing.
3. Stronger and more uniform stacks can be assembled than the method presently employed.
4. Anodes molded directly into the cell cups would reduce the amount of corrosion due to intercell leakage of electrolyte.

Methods of controlling the amount of hydrogen gas generated by the magnesium alloys should be fully exploited. This would include techniques of venting the gas at cell assembly.

# MAGNESIUM CELL (ASSEMBLY)



EXPLODED VIEW

FIGURE 1.

MAGNESIUM FLAT CELL ASSEMBLY.

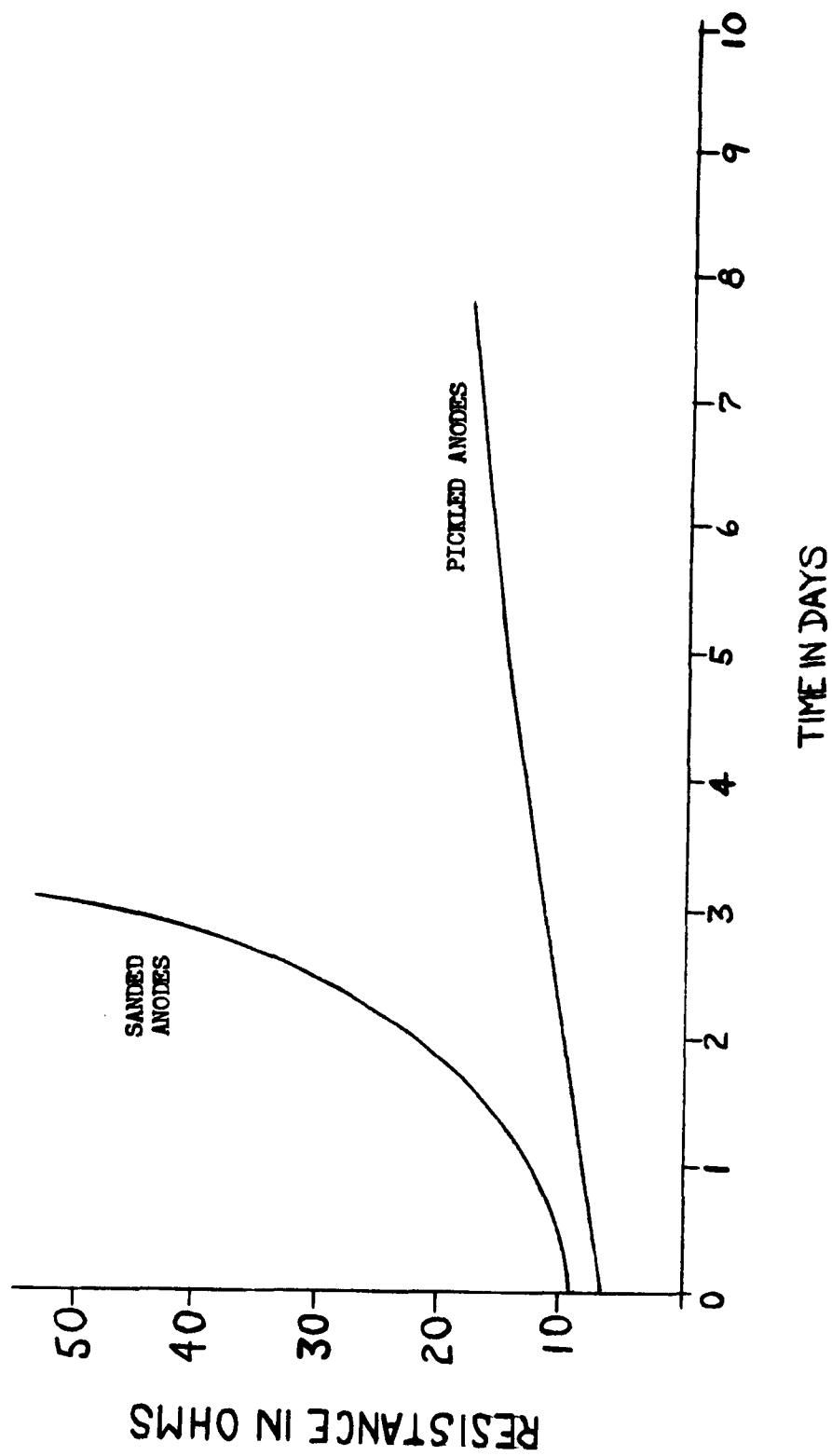


FIGURE 2. EFFECT OF PICKLING SOLUTION ON RESISTANCE OF MAGNESIUM ANODES.



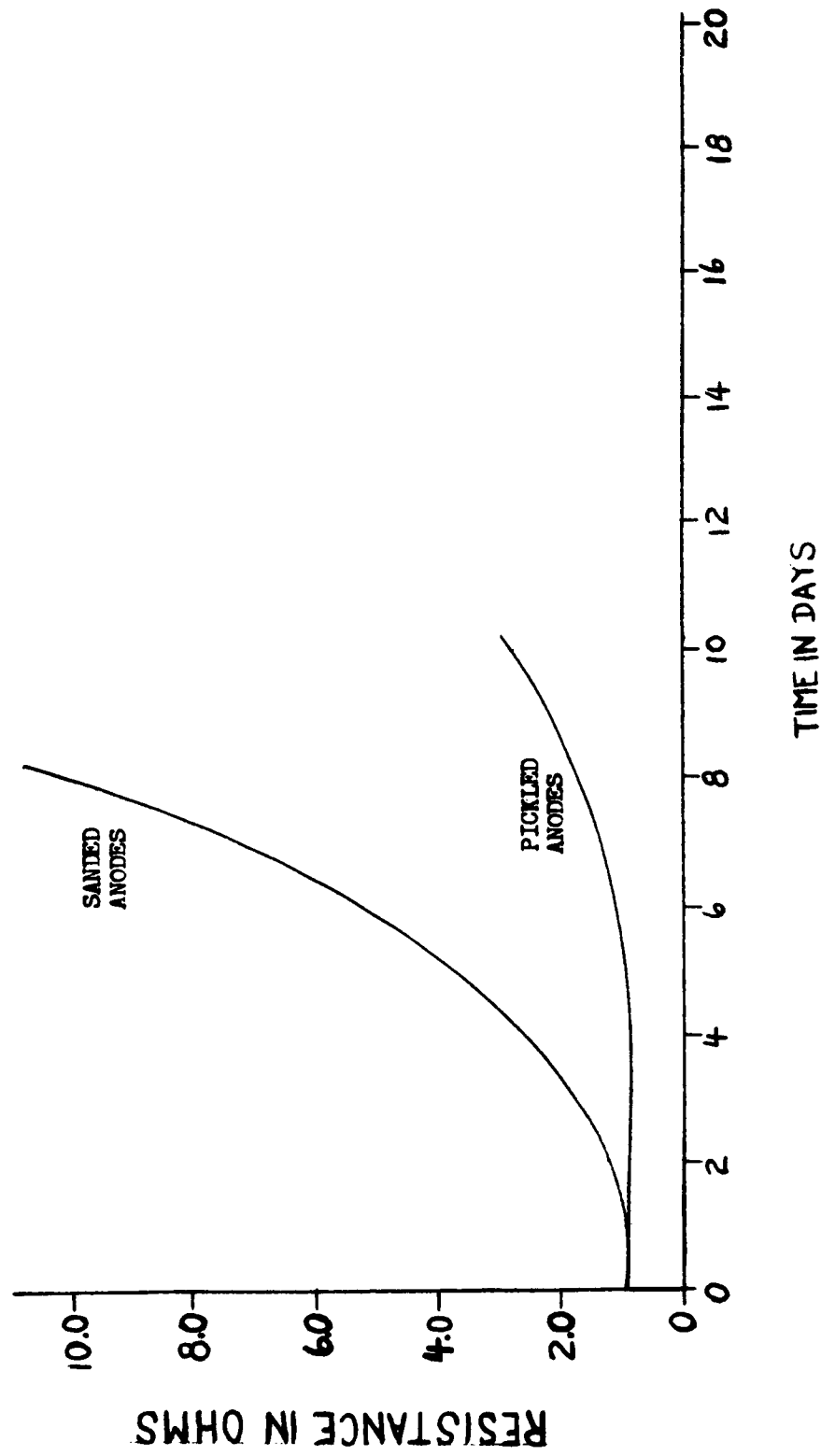


FIGURE 3. EFFECT OF ADHESIVES ON THE RESISTANCE OF MAGNESIUM ANODES WITH VARIOUS TREATMENTS PRIOR TO APPLICATION OF THE ADHESIVE.

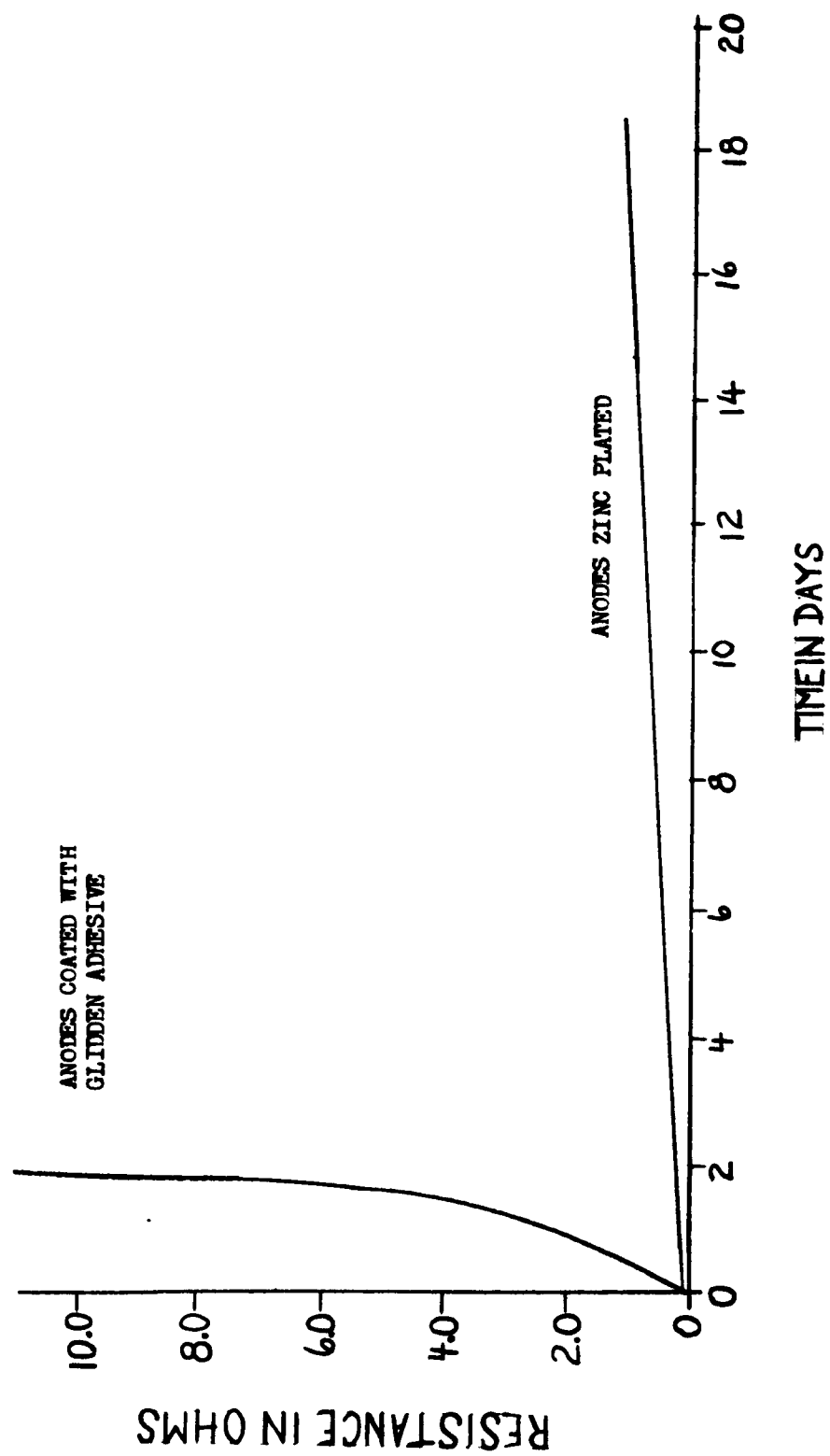


FIGURE 4. EFFECT OF DOW ELECTROPLATING PROCESS ON RESISTANCE OF MAGNESIUM ANODES.

# MAGNESIUM FLAT CELL ASSEMBLY

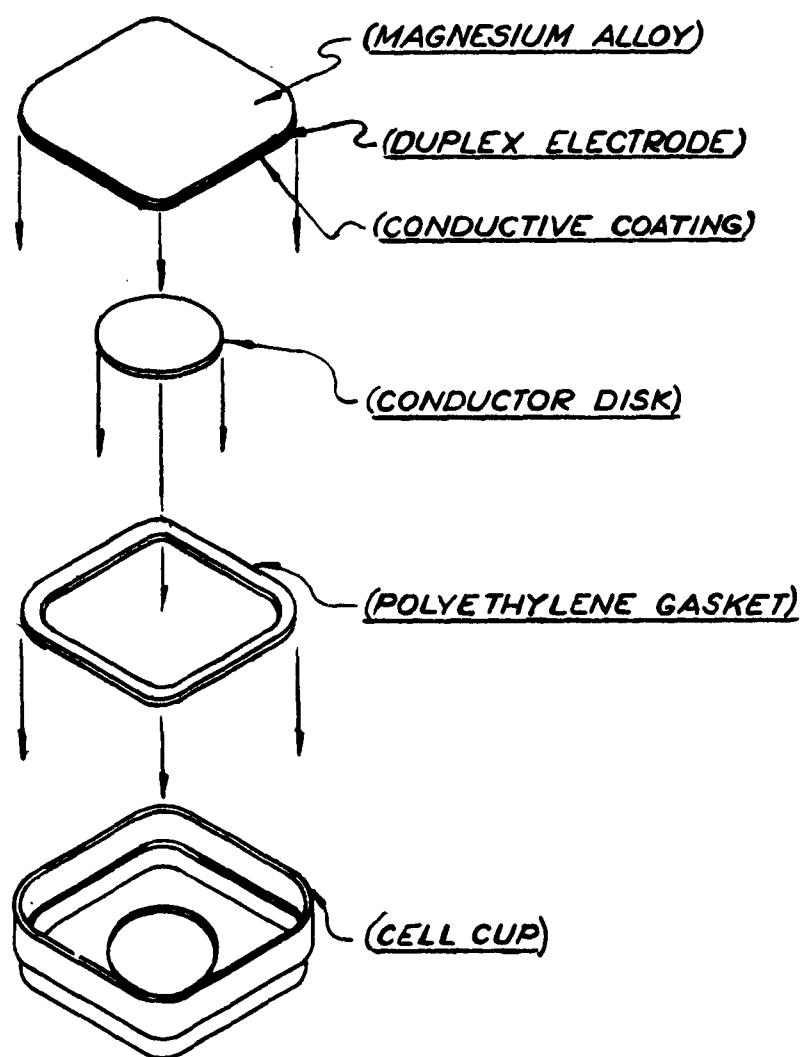


FIGURE 5. DUPLEX ELECTRODE ASSEMBLY WITH POLYETHYLENE GASKET.

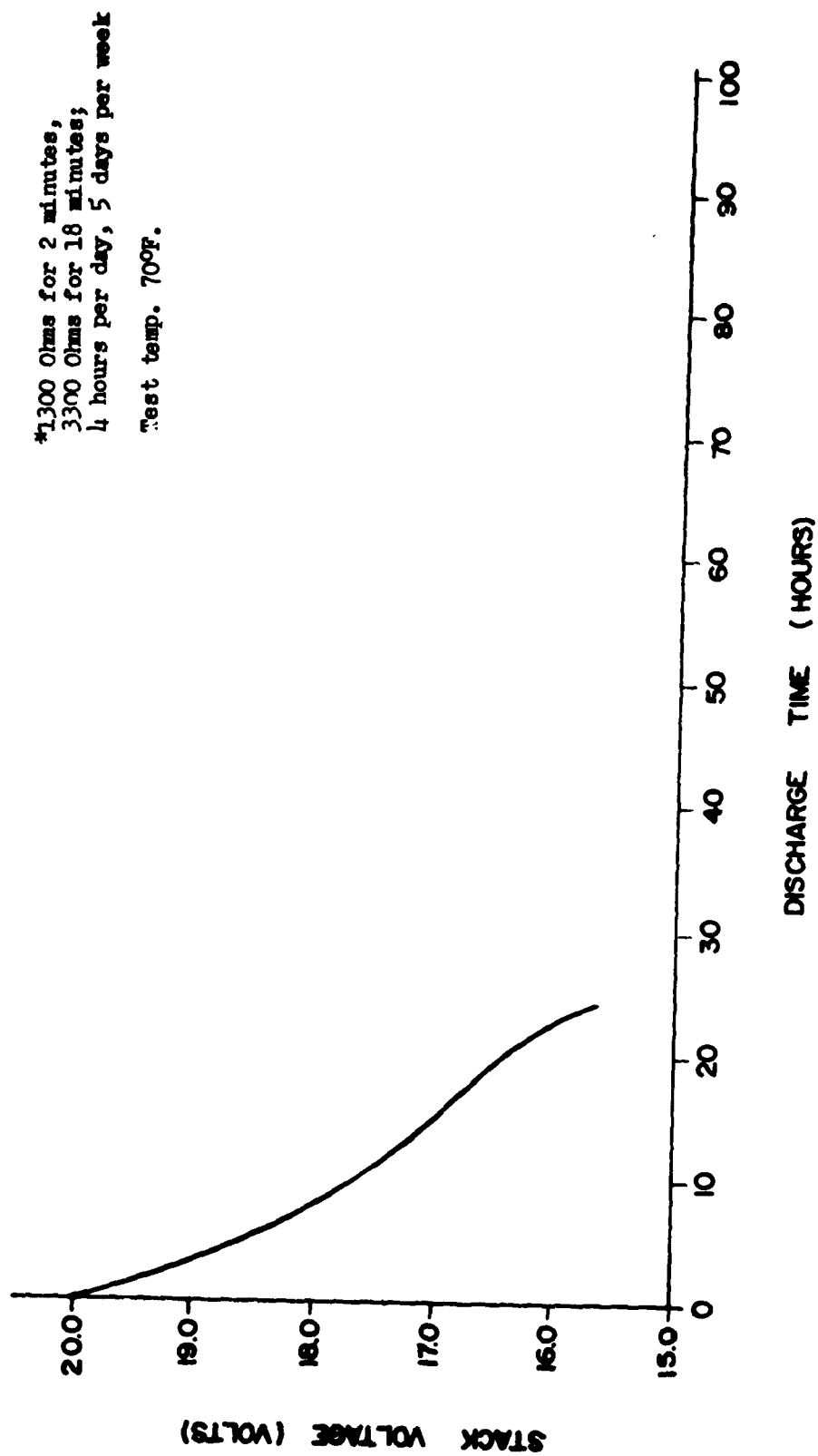


FIGURE 6. INITIAL CAPACITY DATA FOR MAGNESIUM FLAT CELL BATTERIES EMPLOYING NATURAL  $MnO_2$  DISCHARGED AT THE BA-4JL/U DRAIN\*

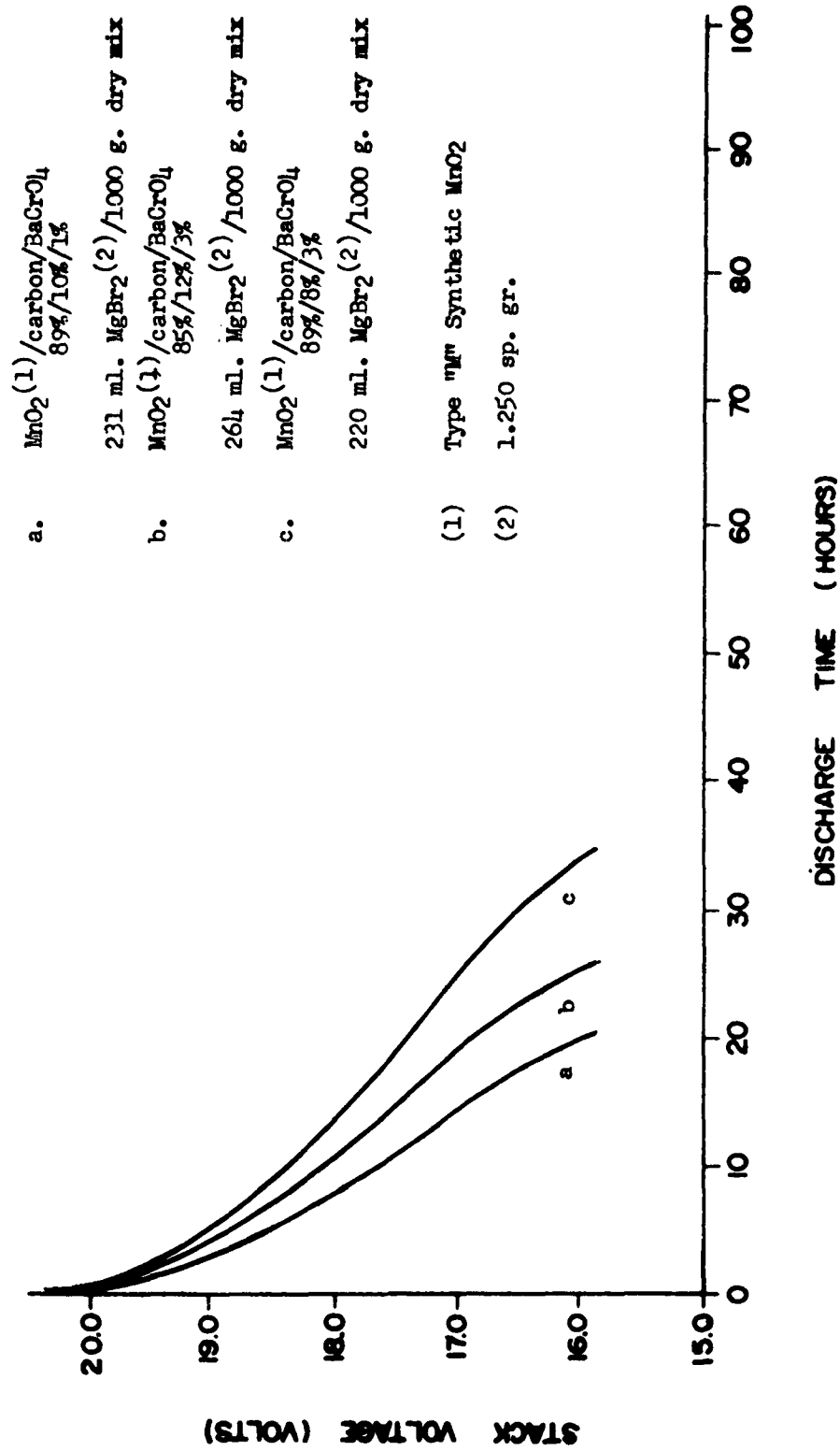


FIGURE 7. INITIAL CAPACITY DATA FOR BATTERIES EMPLOYING VARIOUS CATHODE-MIX FORMULATIONS DISCHARGED AT THE BA-414/U DRAIN\*

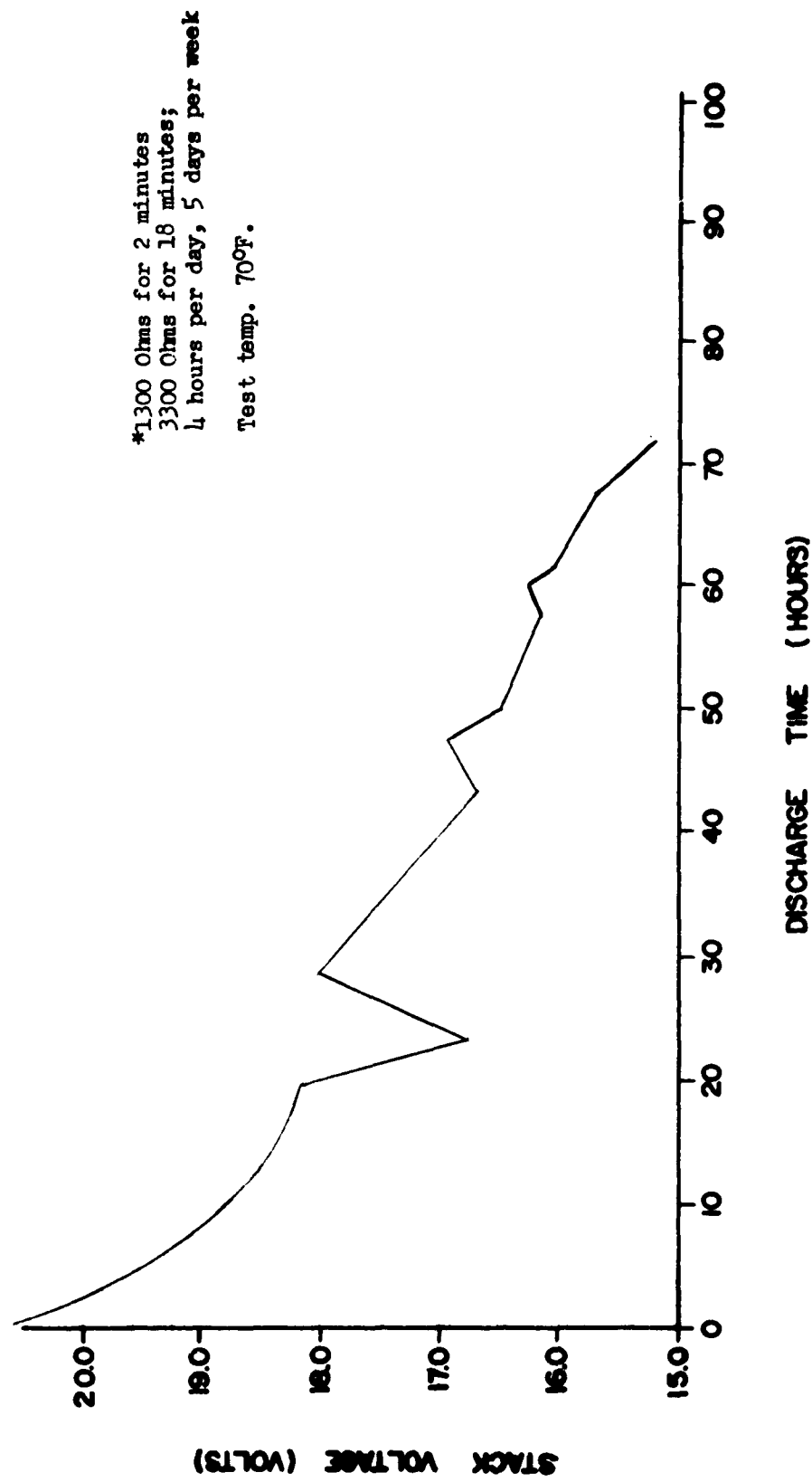


FIGURE 8. INITIAL CAPACITY OF MAGNESIUM FLAT CELL BATTERIES DISCHARGED AT THE BA-4114/U DRAIN\* SHOWING ERRATIC DISCHARGE PERFORMANCE WHICH RESULTS FROM INCONSISTENT HYDROGEN VENTING

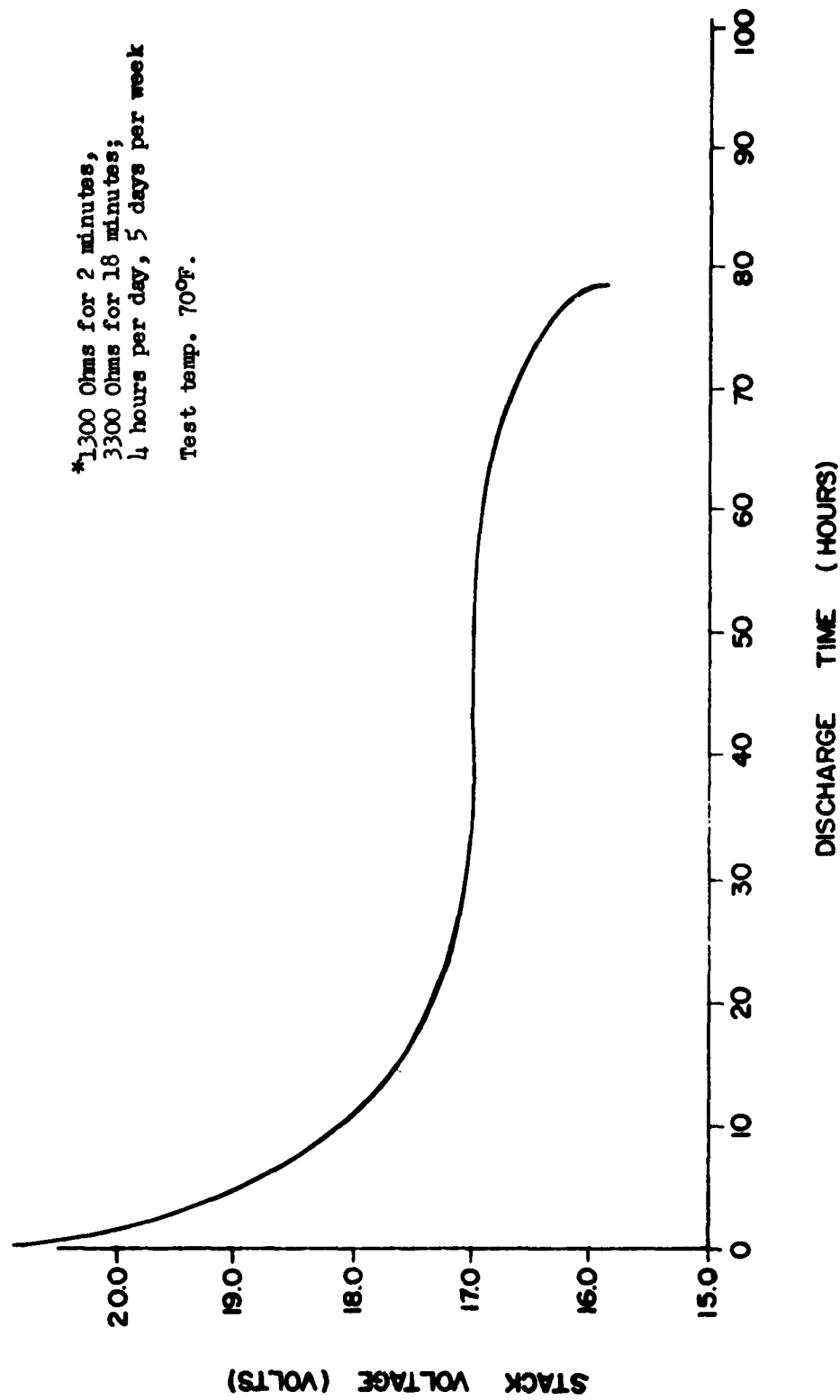


FIGURE 9. EFFECT OF IMPROVED HYDROGEN VENTING UPON THE INITIAL CAPACITY OF  
 MAGNESIUM FLAT CELL STACKS

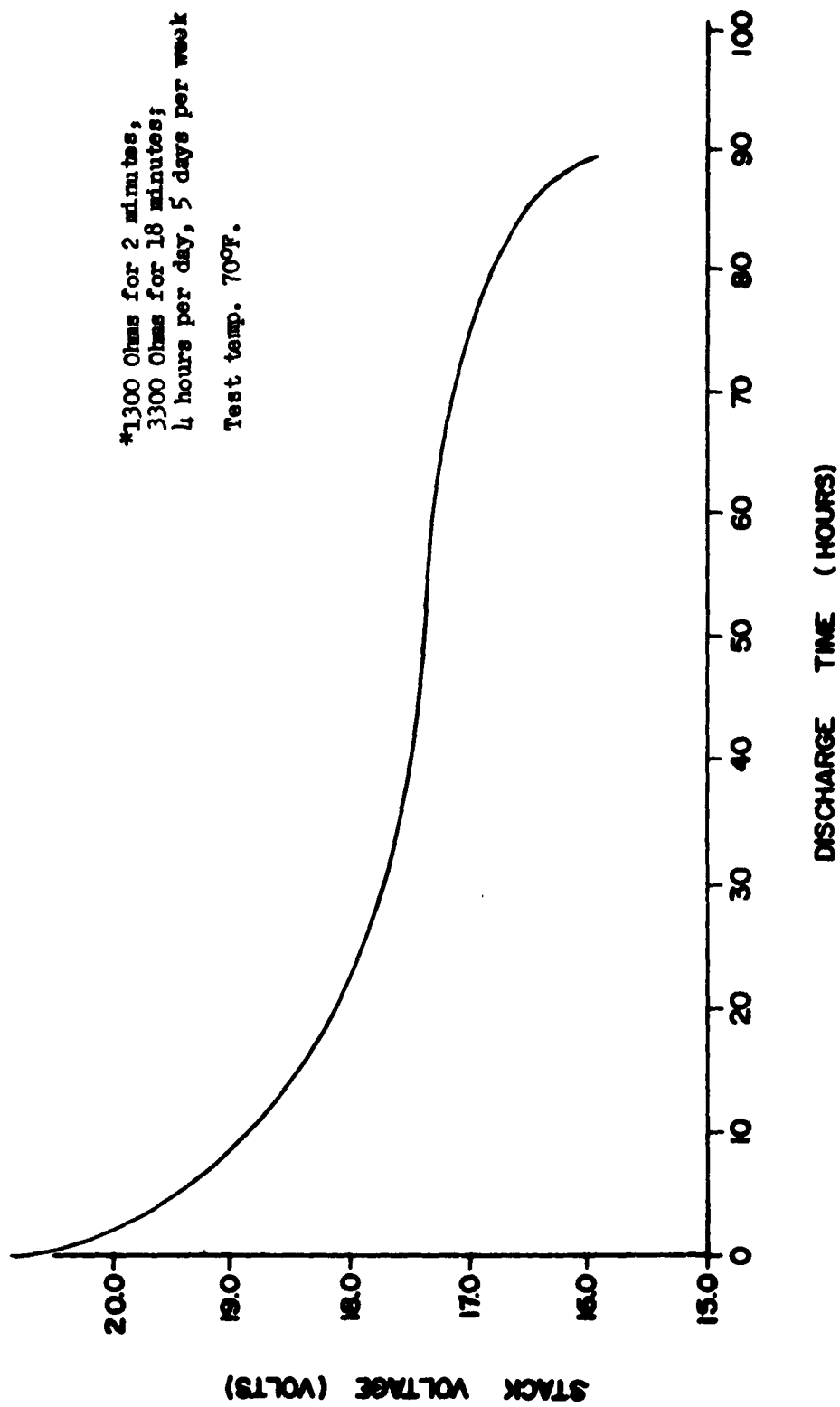


FIGURE 10. EFFECT OF SOLVENT SEALING WITH 10 PERCENT BUTYRATE SOLUTION ON THE INITIAL DISCHARGE CHARACTERISTICS OF MAGNESIUM FLAT CELL BATTERIES.



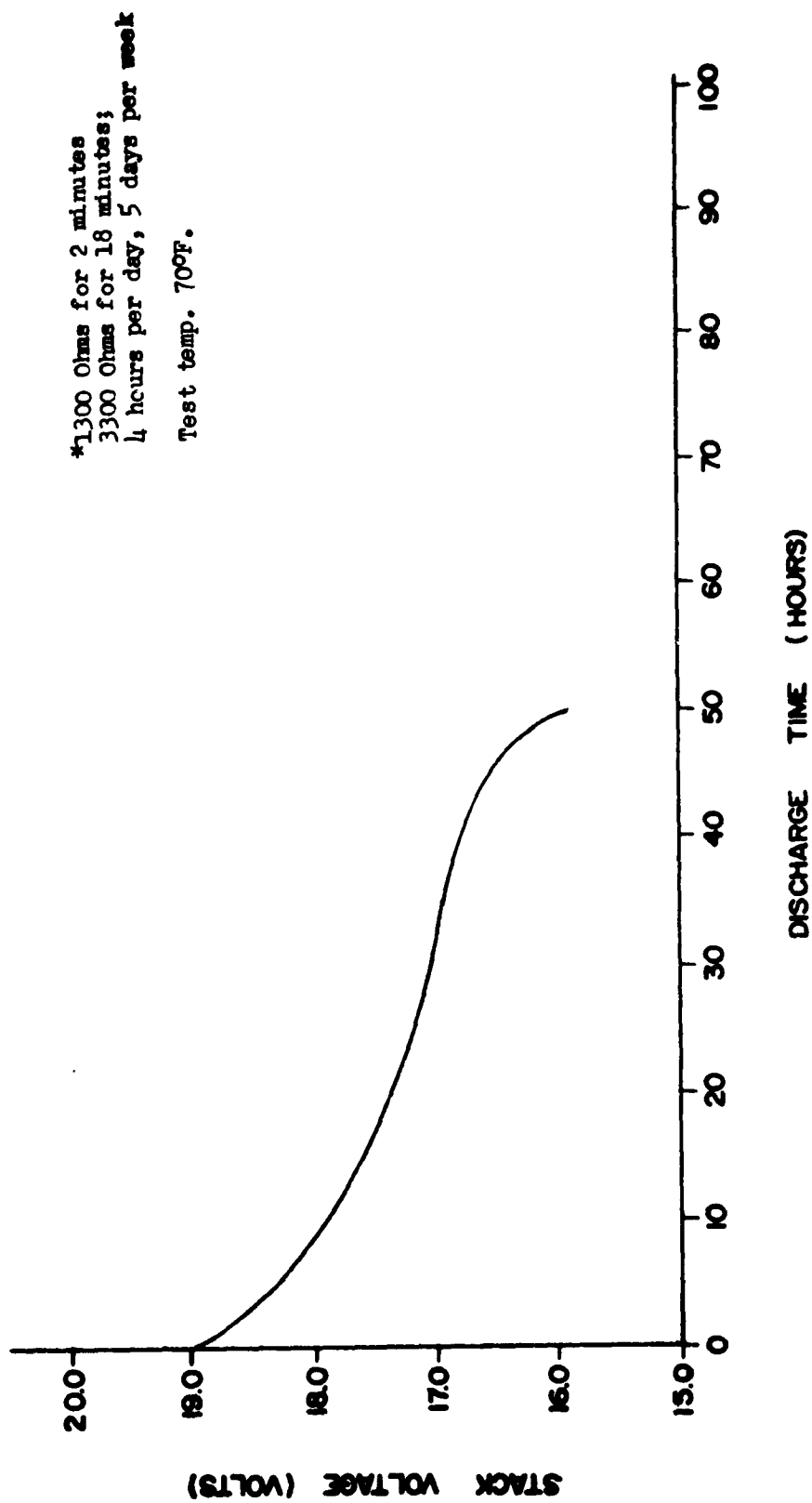


FIGURE 11. EFFECT OF SOLVENT SEALING WITH 10 PERCENT BUTYRATE SOLUTION ON THE DISCHARGE CHARACTERISTICS OF MAGNESIUM FLAT CELL BATTERIES DISCHARGED AFTER 3 MONTHS STORAGE AT 113°F.

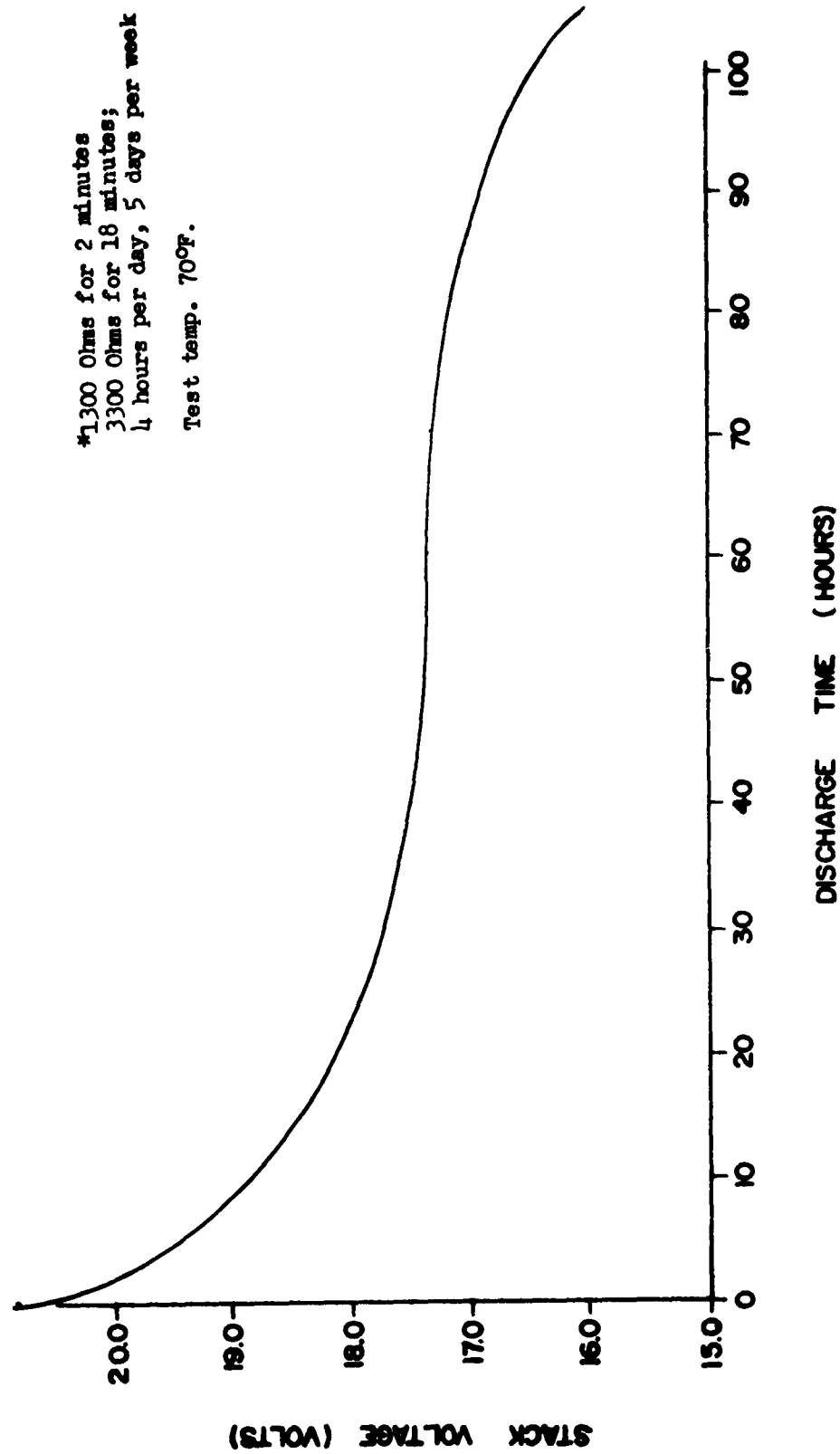


FIGURE 12. INITIAL CAPACITY DATA SHOWING THE MAXIMUM DISCHARGE PERFORMANCE OF MAGNESIUM FLAT CELL BATTERIES DISCHARGED AT THE BA-411/U DRAIN\*

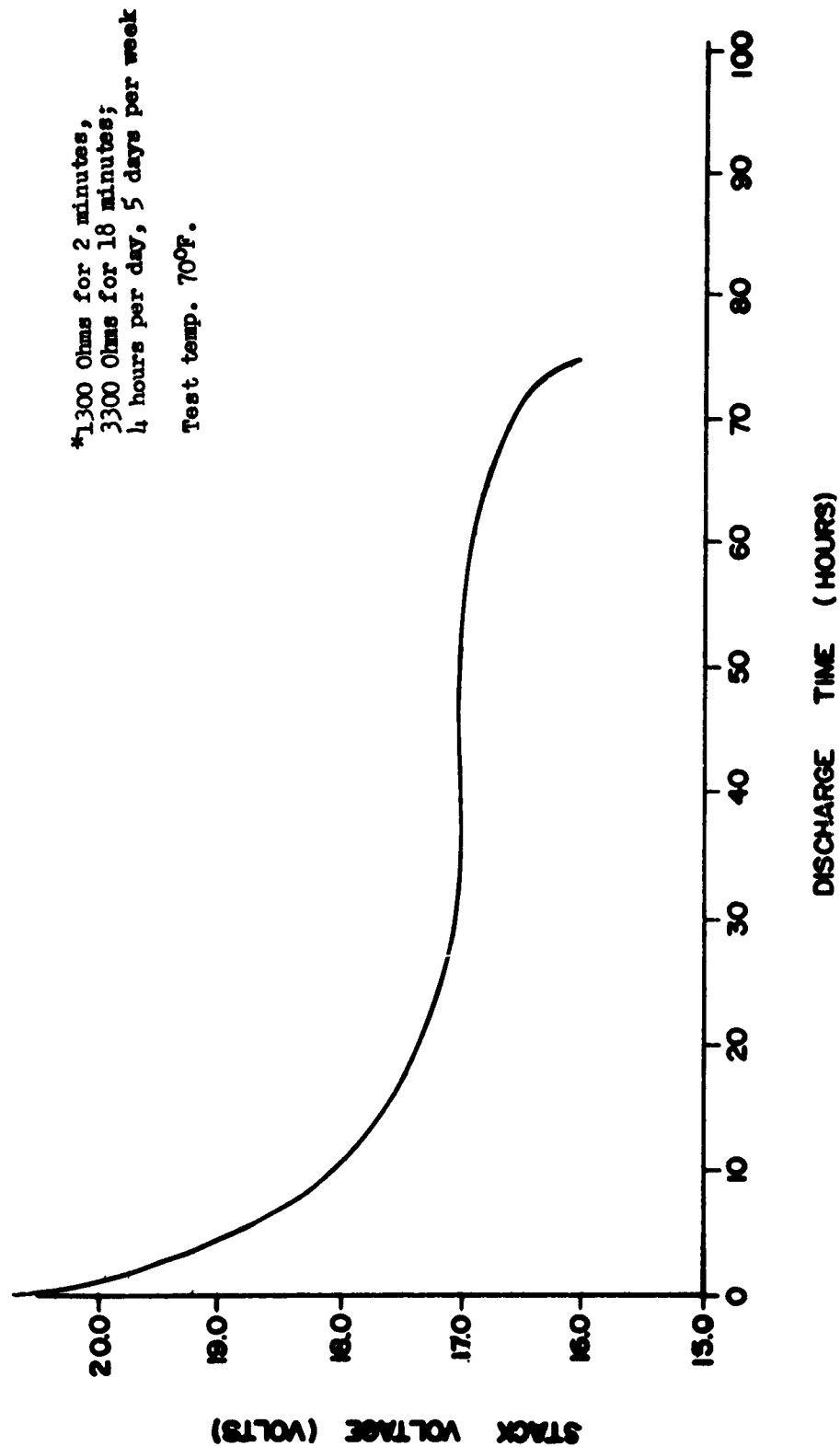


FIGURE 13. EFFECT OF VISCOUS SOLVENT SEALING SOLUTIONS ON THE INITIAL CAPACITY OF MAGNESIUM FLAT CELL BATTERIES DISCHARGED AT THE BA-411/U TRAIN\*

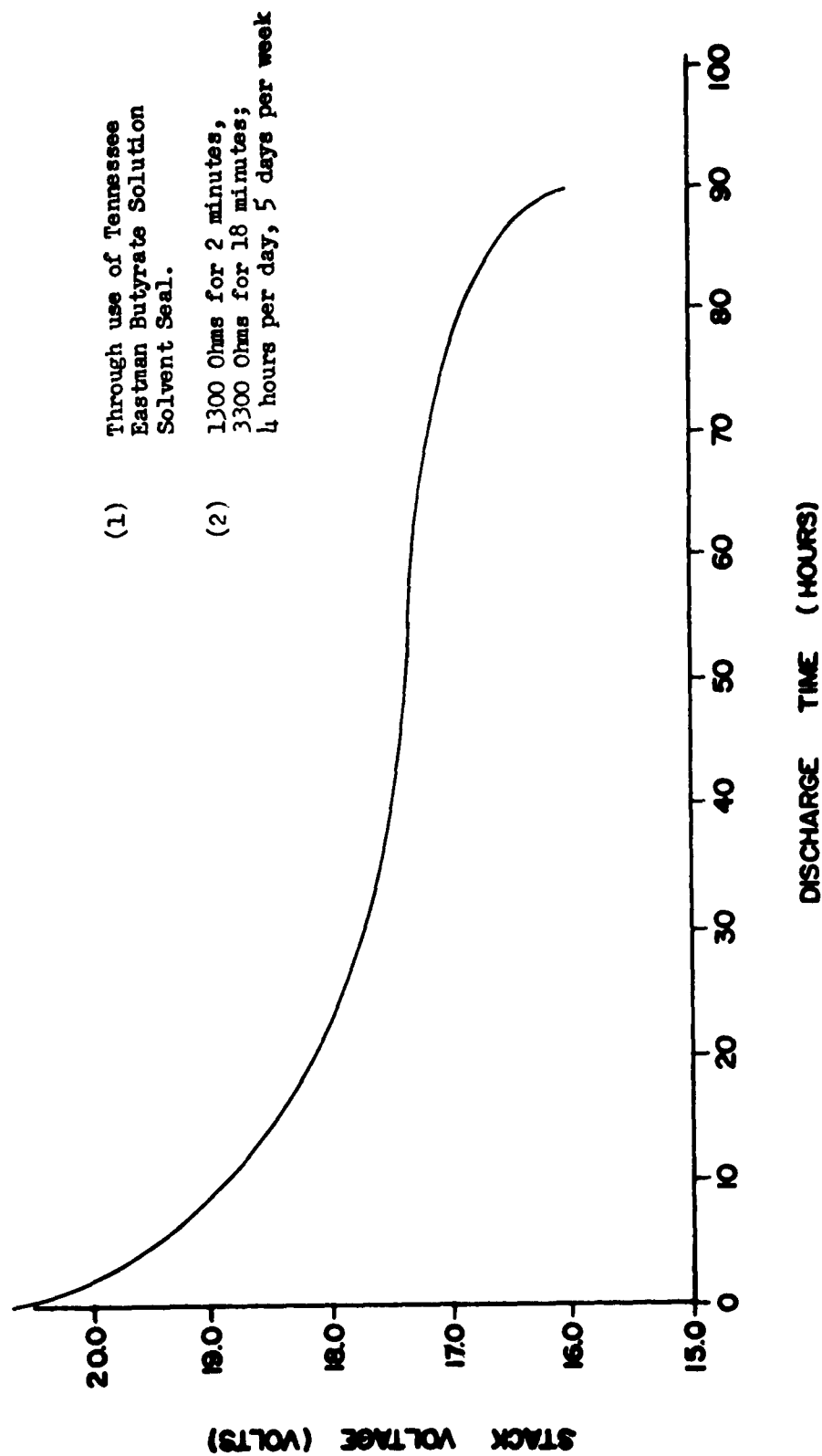


FIGURE 14. EFFECT OF IMPROVED SEALING<sup>(1)</sup> UPON THE INITIAL CAPACITY OF MAGNESIUM FLAT CELL BATTERIES DISCHARGED AT THE BA-414/U DRAIN<sup>(2)</sup> FOR TENNESSEE EASTMAN BUTYRATE SOLUTION SOLVENT SEAL DISCHARGE PERFORMANCE OF MAGNESIUM FLAT CELL BATTERIES

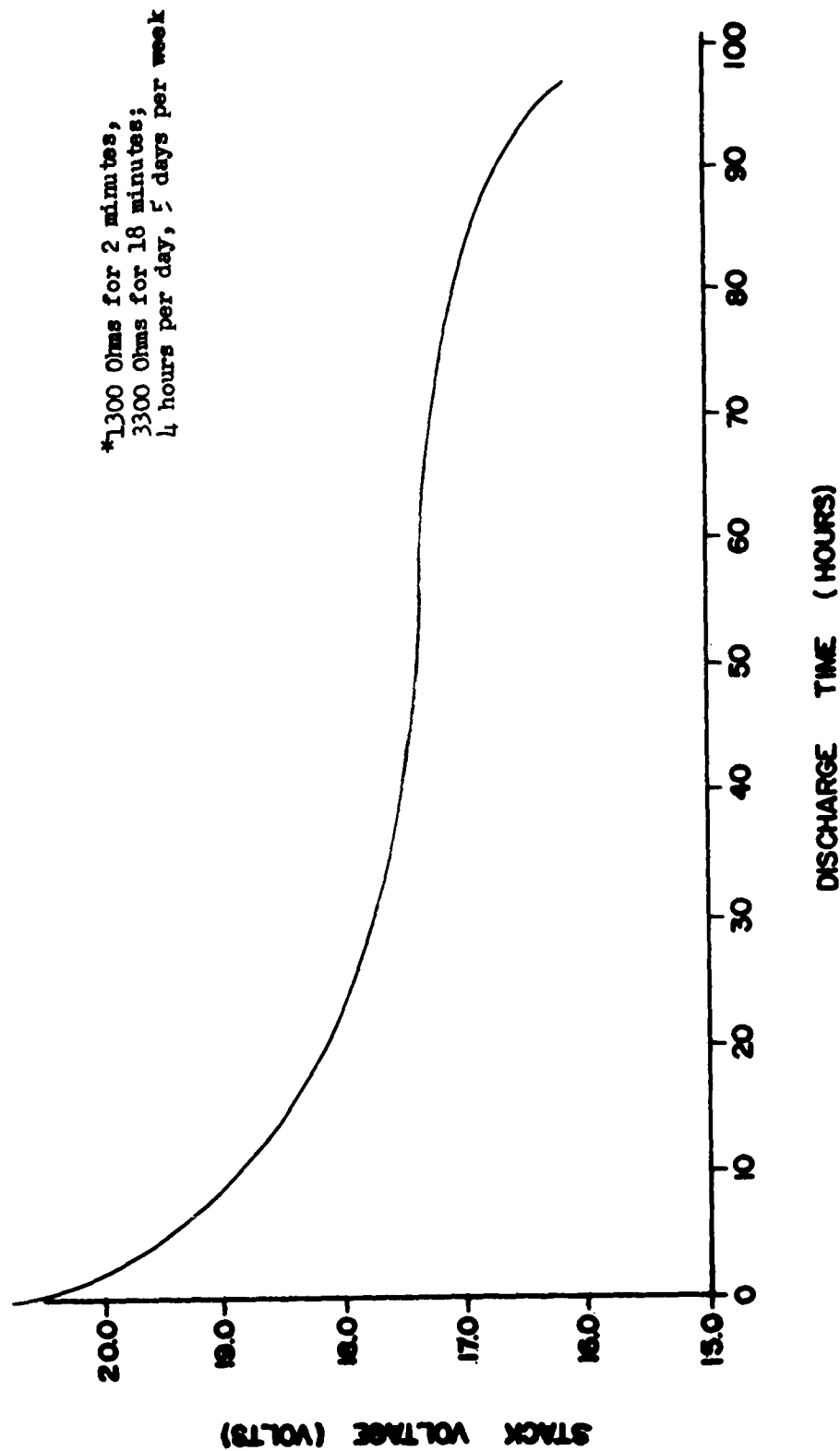


FIGURE 15. EFFECT OF CELL CUPS BONDED WITH GENERAL ELECTRIC SILICONE RUBBER CEMENT ON THE INITIAL DISCHARGE PERFORMANCE OF MAGNESIUM FLAT CELL BATTERIES DISCHARGED AT THE BA-411/U TRAIN\*

READING	OPEN CIRCUIT VOLTAGE (O.C.V.)	SHORT CIRCUIT AMPERAGE (S.C.A.)
Initial	22.6	0.32
	22.6	0.34
	22.5	0.35
4 Days	21.4	0.06
	20.3	0.03
	21.2	0.06
32 Days	9.5	0.05
	7.5	0.05
	10.7	0.05

TABLE I. INITIAL DATA FOR 11-CELL MAGNESIUM  
FLAT CELL BATTERY.

MAGNESIUM BROMIDE ELECTROLYTE 1.100 SP. GR.						
ANODE	READING	INITIAL	14 DAYS	21 DAYS	2 MONTHS	4 MONTHS
AZ10	O.C.V.	22.6	11.0	9.8	3.5	2.0
	S.C.A.	0.55	0.01	0.00	0.00	0.00
AZ21	O.C.V.	22.5	12.5	9.2	4.3	3.0
	S.C.A.	0.60	0.01	0.00	0.00	0.00

MAGNESIUM BROMIDE ELECTROLYTE 1.200 SP. GR.						
ANODE	READING	INITIAL	14 DAYS	21 DAYS	2 MONTHS	4 MONTHS
AZ10	O.C.V.	23.1	15.0	10.0	2.6	1.2
	S.C.A.	1.0	0.01	0.00	0.00	0.00
AZ21	O.C.V.	22.8	17.0	14.0	2.5	1.6
	S.C.A.	0.8	0.01	0.00	0.00	0.00

MAGNESIUM BROMIDE ELECTROLYTE 1.300 SP. GR.						
ANODE	READING	INITIAL	14 DAYS	21 DAYS	2 MONTHS	4 MONTHS
AZ10	O.C.V.	23.0	21.2	20.9	11.5	6.5
	S.C.A.	0.8	0.05	0.03	0.00	0.00
AZ21	O.C.V.	23.0	21.2	20.1	13.5	5.5
	S.C.A.	0.8	0.06	0.03	0.00	0.00

MAGNESIUM BROMIDE ELECTROLYTE 1.400 SP. GR.						
ANODE	READING	INITIAL	14 DAYS	21 DAYS	2 MONTHS	4 MONTHS
AZ10	O.C.V.	25.0	22.4	17.7	22.0	—*
	S.C.A.	0.9	0.18	0.06	0.03	—
AZ21	O.C.V.	25.0	22.4	22.2	22.0	—
	S.C.A.	1.0	0.2	0.18	0.03	—

\*NO READINGS TAKEN DUE TO SEPARATION OF CELL COMPONENTS.

TABLE II. EFFECT OF MAGNESIUM BROMIDE ( $MgBr_2$ )  
ELECTROLYTE CONCENTRATION ON MAGNESIUM  
ANODES.

DAYS AFTER ASSEMBLY	STACK NO. 1		STACK NO. 2		STACK NO. 3		STACK NO. 4	
	Volts	Amps	Volts	Amps	Volts	Amps	Volts	Amps
1	23.0	.70	23.0	.85	23.1	.75	23.0	1.00
2	22.1	.60	22.3	.70	22.6	.64	22.3	.85
6	21.7	.50	21.9	.60	21.8	.50	21.8	.65
9	21.6	.45	21.6	.55	21.6	.40	21.6	.60
10	21.4	.45	20.2	.35	21.4	.35	21.4	.55

TABLE III. OPEN CIRCUIT VOLTAGE AND SHORT CIRCUIT AMPERAGE  
DATA FOR 11 CELL MAGNESIUM FLAT CELL STACKS.



CELL NO.	VOLTAGE	AMPERAGE
1	1.93	.45
2*	0.05	.00
3	1.92	.62
4	1.92	.42
5	1.90	.30
6	1.92	.45
7	1.92	.58
8	1.92	.62
9	1.94	.60
10	1.90	.25
11	1.90	.40

\*CELL NO. 2 FAILED DUE TO ELECTROLYTE PENETRATION  
OF THE CONDUCTIVE LACQUER.

TABLE IV. OPEN CIRCUIT VOLTAGE AND SHORT CIRCUIT  
AMPERAGE DATA FOR INDIVIDUAL CELLS OF  
STACK NO. 2

STACK NO.	1	2	3	4	5	6
READING	O.C.V. VOLTS	S.C.A. MA.	O.C.V. VOLTS	S.C.A. MA.	O.C.V. VOLTS	S.C.A. MA.
INITIAL	22.4	650	22.4	630	22.4	620
5 DAYS	22.1	700	22.1	700	22.2	690
7 DAYS	21.6	650	21.3	600	21.4	500
13 DAYS	21.3	710	21.4	740	21.3	650
					21.5	600
					21.2	700

TABLE V. OPEN CIRCUIT VOLTAGE AND SHORT CIRCUIT AMPERAGE DATA FOR MAGNESIUM  
FLAT CELL STACKS PREPARED WITH DOW CONDUCTIVE LACQUER.

STACK NO.	1*	2	3	4*	5*	6
READING	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.
INITIAL	22.8 1150	22.7 1250	22.4 1000	22.7 1050	22.4 1100	22.7 1005
21 DAYS	18.6 300	21.4 950	21.5 950		21.3 350	21.4 950
33 DAYS		21.4 900	21.4 950			21.0 700
54 DAYS		19.0 800	21.3 600			15.0 002
57 DAYS		16.0 100	12.5 005			

\*STACK NO. 1 - LOW READING DUE TO ELECTROLYTE PENETRATION THROUGH CONDUCTIVE COATING AT CELL WINDOW.

\*STACK NO. 4 - DISSECTED STACK FOR MOISTURE DETERMINATION.

\*STACK NO. 5 - STACK SPLIT AT TWO CELLS DUE TO EXCESSIVE GASSING FROM INTERNAL SHORTING.

TABLE VI. OPEN CIRCUIT VOLTAGE AND SHORT CIRCUIT AMPERAGE DATA FOR MAGNESIUM FLAT CELL STACKS PREPARED WITH DOW NO. 3 CONDUCTIVE COATING.

CELL NO.	OPEN CIRCUIT VOLTAGE (Volts)	SHORT CIRCUIT AMPERAGE (Amps)
1	1.90	.40
2	1.85	.05
3	0.45	.00
4	0.15	.00
5	1.92	.30
6	1.90	.05
7	1.90	.15
8	1.90	.40
9	1.84	.65
10	1.90	.05
11	1.90	.50

\*(AFTER 60 DAYS STORAGE AT 70°F)

TABLE VII. INDIVIDUAL CELL DATA OF STACK\*  
NO. 1 PREPARED WITH DOW NO. 3  
CONDUCTIVE COATING.

STACK NO.	1	2	3	4	5	6
READING	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.	O.C.V. VOLTS S.C.A. MA.
INITIAL	22.4 650	22.0 640	22.4 630	22.4 620	22.2 690	22.3 680
29 DAYS	21.2 600	21.1 620	21.1 650	21.0 400	22.2 550	21.2 650
40 DAYS	21.0 550	21.0 500	19.7 500	21.1 300	21.2 500	21.2 650
61 DAYS	16.4 000	16.0 000	17.0 000	11.0 000	19.2 150	21.2 550
74 DAYS	3.0 000	3.0 000	2.0 000	4.0 000	4.0 000	5.0 000

STACK NO.	1	2	3	4	5	6*	7	8*
READING	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.
3 DAYS	22.8 450	22.8 500	22.9 500	22.8 450	22.6 400	22.7 370	22.7 420	22.7 400
7 DAYS	22.1 400	22.1 400	22.1 420	22.1 400	22.1 350	21.0 050	22.1 360	
14 DAYS	21.8 300	21.8 350	21.8 350	21.8 320	21.8 300		21.7 280	
24 DAYS	21.6 300	21.6 340	21.7 340	21.7 300	21.7 300		21.7 280	
28 DAYS	21.5 290	21.4 310	21.6 310	21.5 300	21.5 260		21.5 260	

\*STACK NO. 6 - LOW SHORT CIRCUIT AMPERAGE DUE TO ELECTROLYTE PENETRATION THROUGH CONDUCTIVE COATING.

\*STACK NO. 8 - DISSECTED FOR RESISTANCE MEASUREMENTS.

TABLE IX. OPEN CIRCUIT VOLTAGE AND FLASH CURRENT DATA FOR MAGNESIUM  
FLAT CELL STACKS ASSEMBLED WITHOUT USE OF PASSLER  
CONDUCTIVE FILM.

STACK NO.	9*	10	11	12	13	14	15	16
READING	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.
3 DAYS	22.9 1050	21.7 980	22.7 1000	22.7 1150	22.8 1070	22.8 960	22.7 980	22.8 1000
7 DAYS		21.1 900	22.1 900	22.1 1120	22.1 950	22.1 940	22.1 900	22.1 1000
14 DAYS		21.7 800	21.8 780	21.7 950	21.8 850	21.8 750	21.8 800	21.8 940
24 DAYS		21.6 750	21.6 750	21.6 890	21.6 820	21.5 690	21.6 780	21.6 900
28 DAYS		21.4 730	21.4 740	21.3 850	21.4 800	21.4 650	21.4 760	21.4 870

\*STACK NO. 9 - DISSECTED FOR RESISTANCE MEASUREMENTS.

TABLE X. OPEN CIRCUIT VOLTAGE AND FLASH CURRENT DATA FOR MAGNESIUM  
FLAT CELL STACKS INCORPORATING FASSLER NO. 2  
CONDUCTIVE FILM.

STACK NO.	1	2	3	4	5	6	7
READINGS	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.	O.C.V. MA.
64 DAYS	21.2 660	21.2 680	21.2 780	21.2 740	21.2 570	21.2 710	21.2 800
102 DAYS	21.2 570	21.1 600	21.0 600	21.2 630	21.1 460	21.2 640	21.1 630
128 DAYS	21.0 500	21.1 550	21.0 450	21.1 550	21.1 400	21.2 570	21.1 520

TABLE XI. OPEN CIRCUIT VOLTAGE AND FLASH CURRENT DATA FOR STACKS  
EMPLOYING FASSLER NO. 2 FILM AND POLYETHYLENE GASKET.



INITIAL		1 MONTH			2 MONTHS			3 MONTHS			STORAGE CONDITIONS	
		16.5	15.0	13.5	16.5	15.0	13.5	16.5	15.0	13.5		
$\bar{X}$	40.2	81.5	97.8	40.8	80.4	100.0	37.0	79.8	98.6	28.2	80.0	98.7
R	1.0	3.0	5.5	2.0	15.5	10.2	9.0	11.0	5.3	37.1	6.0	4.5
$\bar{Y}$	--	--	--	30.6	82.0	101.0	28.1	77.8	100.6	18.6	72.0	102.8
R	--	--	--	1.5	3.0	3.3	6.0	10.0	8.3	22.3	14.0	13.0

3100 OHM CONTINUOUS DRAIN AT INDICATED VOLTAGE CUTOFF.

Capacity in Hours

$\bar{X}$  = Average

R = Range

TABLE XII. INITIAL DISCHARGE AND TROPICAL STORAGE DATA FOR MAGNESIUM  
FLAT CELL STACKS DISCHARGED CONTINUOUSLY  
THROUGH 3100 OHMS.

FLAT CELL STACKS DISCHARGED AT  
(11 CELLS IN SERIES)  
AN EQUIVALENT BA-414/U DRAIN

1300 Ohms for 2 Minutes  
3300 Ohms for 18 Minutes  
4 hours per day  
5 days per week

70°F., 50% RH TO 16.5 VOLT CUTOFF				
	INITIAL	1 MONTH	2 MONTHS	3 MONTHS
$\bar{X}$	26.0	26.3	19.0	18.0
R	6.7	1.0	8.0	12.0

113°F., 50% RH TO 16.5 VOLT CUTOFF				
	INITIAL	1 MONTH	2 MONTHS	3 MONTHS
$\bar{X}$	16.0	18.3	7.9	9.5
R	12.0	9.0	12.3	13.5

Capacity in Hours

$\bar{X}$  = Average

R = Range

TABLE XII. SHELF LIFE DATA FOR STACKS DISCHARGED  
AT AN EQUIVALENT BA-414/U DRAIN

FLAT CELL STACK DISCHARGED  
(11 CELLS IN SERIES)  
CONTINUOUSLY THROUGH 3100 OHMS

LOT NO.	CATHODE-MIX FORMULATION	MnO <sub>2</sub>	INITIAL
A	89-10-1	Type "M"	$\bar{X}$ 30.4 R 5.0
B	85-12-3	Type "M"	$\bar{X}$ 30.2 R 82.3
C	89-8-3	Type "M"	$\bar{X}$ 39.3 R 75.0

70°F., 50% RH - 16.5 VOLT CUTOFF

Capacity in Hours

$\bar{X}$  = Average

R = Range

TABLE XIV. INITIAL CAPACITY DATA FOR MAGNESIUM  
FLAT CELL STACKS EMPLOYING VARIOUS  
CATHODIC FORMULATIONS.

LOT NO.	CATHODE-MIX FORMULATION	MnO <sub>2</sub>	INITIAL
A	89-10-1	Type "M"	$\bar{X}$ 20.0 R 12.0
B	85-12-3	Type "M"	$\bar{X}$ 30.2 R 82.3
C	89-8-3	Type "M"	$\bar{X}$ 39.3 R 68.0

70°F., 50% RH - 16.5 VOLT CUTOFF

\*11 FLAT CELLS IN SERIES

Capacity in Hours

$\bar{X}$  = Average

R = Range

TABLE IV. CAPACITY DATA FOR STACKS\* EMPLOYING CATHODE-MIX FORMULATIONS DISCHARGED AT AN EQUIVALENT BA-414/U DRAIN.

FLAT CELL STACKS DISCHARGED AT EQUIVALENT BA-4114/U DRAIN  
 1300 Ohms for 2 Mins., 3300 Ohms for 18 Mins.,  
 4 Hours Per Day, 5 Days Per Week

70 F., 50% RH - 16.5V		13 F., 50% RH-16.5V		
INITIAL		1 MONTH	2 MONTHS	3 MONTHS
58.3	✓	19.5	16.5	29.0
44.0	R	88.0	88.0	55.6

STACKS CONSISTED OF 11 CELLS IN SERIES

Capacity in Hours

$\bar{X}$  = Average

R = Range

TABLE XVI. SHELF LIFE DATA FOR MAGNESIUM STACKS USING BRIGHT STAR  
 ELECTROLYTIC MnO<sub>2</sub>.

		70°F., 50% RH - 16.5V			113°F., 50% RH - 16.5V	
FORMULA		INITIAL	1 MONTH	2 MONTHS	1 MONTH	2 MONTHS
89-10-1	$\bar{X}$	20.0	18.0	16.3	16.3	14.7
Type "M" MnO <sub>2</sub>	R	12.0	10.0	8.0	4.0	12.0

STACKS CONSISTED OF 11 CELLS IN SERIES

Capacity in Hours

$\bar{X}$  = Average

R = Range

TABLE XVII. CAPACITY DATA FOR MAGNESIUM BATTERIES USING TYPE "M"  
MnO<sub>2</sub> DISCHARGED AT THE EQUIVALENT BA-J114/U DRAIN

SOLVENT SEAL	CUP MATERIAL	WETNESS %	INITIAL
ETHYL ACETATE 6 SECOND DIP	CELLULOSE ACETATE BUTYRATE	32.8	$\bar{X}$ 146.0 R 70.0
ETHYL ACETATE 6 SECOND DIP	ETHYL CELLULOSE	32.7	$\bar{X}$ 52.0 R 20.0
ETHYL ACETATE 3 SECOND DIP-10MINUTE AIR DRY-3 SECOND DIP	CELLULOSE ACETATE BUTYRATE	29.6	$\bar{X}$ 59.0 R 68.7
ETHYL ACETATE 3 SECOND DIP-10MINUTE AIR DRY-3 SECOND DIP	ETHYL CELLULOSE	30.6	$\bar{X}$ 67.0 R 25.0
ETHYL ACETATE 9 SECOND DIP	CELLULOSE ACETATE BUTYRATE	31.3	$\bar{X}$ 79.0 R 8.0
ETHYL ACETATE 9 SECOND DIP	ETHYL CELLULOSE	31.0	$\bar{X}$ 69.0 R 10.0

STACKS CONSISTED OF 11 CELLS IN SERIES

Capacity in Hours

$\bar{X}$  = Average

R = Range

TABLE XVIII. INITIAL CAPACITY DATA FOR MAGNESIUM FLAT CELL STACKS EMPLOYING VARIOUS SOLVENT SEALING CONDITIONS.

AD No. \_\_\_\_\_  
Accession No. \_\_\_\_\_  
Bright Star Industries  
Clifton, New Jersey

Unclassified  
1. Magnesium  
Dry  
Batteries  
2. Cells

Flat Cell Mg Dry Cell Batteries  
By J. Davis and R. Pette  
Final Report 30 September 1958 to 30 October 1963  
35 Pages including 15 illustrations and 19 tables  
Signal Corps Contract No. DA-36-039-SC-78231  
Task No. 1G6 22001 A 053-02, Unclassified  
The development and progress of the flat cell  
magnesium batteries by Bright Star Industries,  
Clifton, New Jersey are presented.  
Conductive coating of magnesium alloys, cathode  
mix formulations, duplex electrode and cell  
assembly techniques were investigated.  
Maximum initial service of 100 hours on BA-4114/U  
drains is attributed to adequate hydrogen venting  
of the cell assembly.

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Accession No. \_\_\_\_\_  
Bright Star Industries  
Clifton, New Jersey

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